

**U.S. DEPARTMENT OF COMMERCE
National Technical Information Service**

N77-81135

DISPOSAL OF HYPERGOLIC PROPELLANTS

Florida Institute of Technology
Milbourne, FL

Nov 74

PREFACE

This study was conducted by Florida Institute of Technology under Contract NAS 10-8399, administered by the National Aeronautics and Space Administration, John F. Kennedy Space Center, Florida. The NASA Technical Representative for the contract was Mr. Harold H. Franks, DD-MDD, and the Alternate Technical Representative was Mr. Jimmy L. Dobson, DD-MDD. Florida Institute of Technology's study manager was Dr. Thomas E. Bowman, Mechanical Engineering Department.

The authors gratefully acknowledge the many contributions of Mrs. Lynn Harris in the preparation of this report.

We are also most grateful for the generous assistance, information, and suggestions provided by the many individuals and organizations contacted during the course of this study. Lists of the cooperating organizations are included in the portion of this report covering the "Current State of the Art".

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TABLE OF CONTENTS

	PAGE
Preface	i
Contents	ii
SUMMARY REPORT	1
THE CURRENT STATE OF THE ART (PHASE 1)	24
EVALUATION OF CURRENT DISPOSAL METHODS (PHASE 2)	60
ALTERNATIVE DISPOSAL CONCEPTS (PHASE 3)	161
APPLICATION STUDIES (PHASE 3)	228
Appendix A: Vapor Pressure and Dissociation Curves	306
Appendix B: Monomethyl Hydrazine (MMH) Assay	310
Appendix C: Notes on Scrubbers	311
Appendix D: Special Notes on HF Removal from Effluent Streams	331

SUMMARY REPORT

	Page
I. Introduction	2
II. Significant Results	4
A. Phase 1	4
B. Phase 2	9
C. Phase 3	18
III. Recommendations for Further Study	22

1. INTRODUCTION

Many aerospace launch vehicles and spacecraft utilize hypergolic propellants which are toxic and corrosive, and require special storage, loading and waste disposal systems. The waste disposal systems, for both liquid and vapors, are of especial concern due both to problems of maintaining the quality of the environment, and the changing nature of launch operations that will accompany the advent of the Space Shuttle.

The purpose of this study was to review and evaluate existing propellant disposal methods, to define and investigate new methods where appropriate, and to perform application studies on the implementation of various disposal concepts for Space Shuttle requirements. The specific waste products of concern were liquids and vapors of the following seven hypergolic propellants:

- (1) Nitrogen Tetroxide ($\text{N}_2\text{O}_4 - \text{NO}_2$)
- (2) Inhibited Red Fuming Nitric Acid (IRFNA, $\text{HNO}_3 + \text{NO}_2$
 $+ \text{H}_2\text{O} + \text{HF}$)
- (3) Hydrogen Peroxide (H_2O_2)
- (4) Anhydrous Hydrazine (N_2H_4)
- (5) Monomethyl Hydrazine (MMH, $\text{CH}_3\text{N}_2\text{H}_3$)
- (6) Unsymmetrical Dimethylhydrazine (UDMH, $(\text{CH}_3)_2\text{N}_2\text{H}_2$)
- (7) Aerozine 50 (50% N_2H_4 - 50% UDMH)

The study was divided into three phases. Phase 1 had as its purpose identification of the current, state-of-the-art liquid and vapor disposal methods for these seven propellants. Included were a literature search, contacting manufacturers and users of the propellants, contacting manufacturers of waste disposal equipment, and compilation of the accumulated information in a form suitable for evaluation in Phase 2. We were concerned with the

techniques currently practiced or recommended by manufacturers and users of the specified hypergolic propellants for disposing of contaminated and waste liquids and vapors, and also those techniques which had been discarded for one reason or another, and drawing board ideas being developed. Phase 1 was not an environmental study, and was not directly concerned with the effect of any of these disposal methods on the environment. Rather, it was an engineering study concerned with learning the technical details of the equipment and procedures used by various organizations for hypergolic propellant disposal.

Phase 2 was concerned with evaluation of these current disposal methods, primarily in terms of their effect on the environment. Even here, the emphasis was on identifying requirements for new technology and methods suitable for continued use, rather than on identifying any specific current environmental problems. Economic factors were also taken into account.

The original intention was that Phase 3 concentrate on disposal problems for which current methods are not acceptable for continued use--within the context of prolonged use and increased use rates. The Phase 2 evaluations indicated, however, that while some individual methods are not acceptable for continued use, acceptable methods do exist for disposing of all of the hypergolic propellants, both in liquid and vapor phases. For this reason there was some change of emphasis from the original plan, with major effort devoted to new alternative disposal concepts that might offer substantial benefit relative to existing acceptable disposal methods. In addition, studies of some of the existing methods were carried a step farther to consider design criteria and provide additional guidelines for future designers; and specific shuttle-related disposal requirements at KSC and contingency landing sites were studied.

Our Final Report is presented in five major sections. This section, the Summary Report, is intended to be a concise presentation of the important results of the study. Following sections present the detailed results of each of the three phases of the study, with two sections devoted to Phase 3 because of the eventual broad scope of that portion of the study, and the extensive and diverse nature of the results.

II. SIGNIFICANT RESULTS

A. PHASE I

Our purpose in Phase 1 was to ascertain and catalog what is currently being done to dispose of hypergolic propellants. To this end we contacted chemical manufacturers, users of propellants, disposal equipment manufacturers, and assorted organizations we felt might have suggestions regarding this problem.

We found that the most widespread means of treating all of the listed propellants for disposal is dilution followed by neutralization. Wherever possible, both fuels and oxidizers are transferred to the same holding ponds to be neutralized. Hydrazine and N_2O_4 vapors are often vented to water scrubbers, and the contaminated water is then transferred to the same holding ponds. Incinerators are used for hydrazine liquid wastes, and flare burners for N_2O_4 vapors. N_2O_4 liquid can be allowed to vaporize at atmospheric pressure and disposed through a scrubber or flare burner. Open pit burning is still used to some extent for hydrazines, and is recommended by some authorities, subject to certain precautions. Vapors - both fuel and oxidizer - are commonly vented to the atmosphere.

The hydrazines seem to be regarded by most organizations as the substance presenting the most serious disposal problem. Methods of disposal for the nitrogen-based oxidizers were found to be less elaborate and rigorous. Hydrogen peroxide disposal is a relatively minor problem.

In addition to destructive disposal, there were found to be possibilities for recycling some of the waste propellants, and for converting others to useful purposes. Use of the oxidizers to produce fertilizer seems feasible, and the hydrogen peroxide could be a valuable oxygen source in sewage treatment, and is also being considered as a replacement for chlorine in the later stages of water treatment.

Detailed results of the study are recorded in the section of this report devoted to the "Current State of the Art." Included there are both current practices and recommendations from various sources. The following paragraphs present these results in a more succinct fashion, rather than separating the

information according to source. Here the propellants will be divided into four categories: hydrazines, hydrogen peroxide, nitrogen tetroxide, and inhibited red fuming nitric acid. The reason for combining the hydrazines is that the differences in disposal methods between the various hydrazines were so minor that there is little reason to discuss them separately. Detailed thermochemical descriptions of the various disposal methods are presented later in this report, in the section devoted to "Evaluation of Current Disposal Methods."

II.A.1. Hydrazines

a. Incineration

Two organizations are currently incinerating aqueous solutions of hydrazines (and, in one particular instance, a solution of MMH in isopropyl alcohol). One incinerator uses natural gas as primary fuel and maintains a flame temperature of 1900 F; the other uses diesel fuel and maintains 2700 F or higher (3200 F was also mentioned).

A third organization has developed (and is marketing) a more specialized incinerator capable of disposing of raw liquid hydrazine. A research program carried out under Air Force sponsorship demonstrated the effectiveness of this incinerator in disposing of the hydrazine cleanly and efficiently, with acceptably low formation of oxides of nitrogen and other undesirable products.

An extensive study¹ of the disposal of hazardous wastes (hereafter referred to as "the TRW study") recommended controlled incineration for the disposal of hydrazine, with effluent scrubbing to eliminate any ammonia formed in the combustion process.

b. Neutralization

A number of organizations dispose of hydrazines by dilution followed by neutralization. The manufacturers recommend neutralization using calcium

¹R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy, and C. C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste." Report No. 21485-6013-RU-00, TRW Systems Group, 1 February 1973, prepared for Environmental Protection Agency, Contract No. 38-03-0089. (See especially Vols. I, XII).

hypochlorite or a dilute solution of hydrogen peroxide, catalyzed by a trace amount of copper sulfate. Dilute hydrochloric or sulfuric acid is also recommended in the case of MMH, and atmospheric oxygen in the presence of copper salts for N_2H_4 .

The catalyzed hydrogen peroxide reaction is currently being used by several of the organizations contacted, but not, as far as we could ascertain, the hydrochloric or sulfuric acid reactions. Two organizations precede the hydrogen peroxide reaction with a sodium hydroxide reaction, and at least one uses sodium hydroxide alone to treat dilute hydrazine wastes. Also used for neutralization purposes are dilute nitrogen tetroxide, sodium hypochlorite, and hydroxyacetic acid. Nitrogen tetroxide is used quite commonly since the same holding ponds are used for both fuel and oxidizer wastes.

Hydrazine vapors are often sent through water-spray scrubbers, and the water then treated by one of these neutralization reactions.

c. Air Oxidation and Decomposition

Diluted with water and left in a holding pond, hydrazine will gradually decompose as a result of air oxidation and bacterial action. This process was a little difficult to separate from chemical neutralization in evaluating the results of the survey, since it inevitably occurs whenever hydrazine is present in a holding pond and it is quite likely that even if neutralization is the "official" disposal method, operators will have learned that less chemical is required if it is not added too hastily.

Decomposition can be speeded by use of a catalyst, such as copper sulfate or iron oxide, and by aeration - either bubbling air through the pond, or spraying water from the pond into the air in a fountain. At least two organizations are using aeration ponds of the former type to decompose hydrazine, and another is experimenting with a spray pond. All three use catalysts in conjunction with the aeration.

d. Catalytic Decomposition

In addition to the use of catalysts to speed reactions in dilute solutions, it is also possible to use catalysts directly to speed

the decomposition of raw N_2H_4 and MMH liquids, and of vapors. Such catalysts would be expected to be relatively expensive, although not nearly so expensive as one catalyst used in hydrazine monopropellant thrusters and auxiliary power units. Nickel catalysts at approximately \$5 per pound are most commonly mentioned, and the TRW study mentions the possibility of a new low-cost catalyst that might merit further study; this catalyst, we learned, is molybdenum based.

Although copper sulfate and iron oxide are commonly used as catalysts in holding ponds, direct catalytic decomposition of undiluted liquids or vapors is not currently being employed, as far as we could ascertain.

e. Open Pit Burning

Open pit burning is recommended by the manufacturers for disposal of large quantities of hydrazines, and is still in fairly widespread use, although it seems to be much less prevalent now than several years ago. The TRW study labeled this method "generally acceptable" but warned of excessive NO_x generation. Concentrations less than 40% are not combustible at atmospheric temperatures.

f. Other Methods

Direct reaction of undiluted hydrazine with undiluted N_2O_4 has been used by at least two organizations. Mixing small quantities of slightly out-of-specification hydrazine with large amounts of non-contaminated hydrazine is an alternative to disposal where the volumes are large enough to make this feasible. Filtration to remove suspended particulate matter can also return hydrazine to specification. Return to a chemical company is a possibility. Venting of vapors to the atmosphere is common, often with more or less elaborate precautions, including consideration of mixing models, etc. Dilution followed by pouring on the ground is used, but probably not to any great extent.

II. A. 2. Hydrogen Peroxide

Neither the manufacturers nor the TRW study recommends anything more elaborate than dilution with water and pouring on the ground or into a drainage

system, and these procedures are commonly followed. One organization speeds the decomposition using a catalyst - either platinum or silver screen in the case of small quantities, or NaOH for larger quantities.

Disposal of significant quantities of H_2O_2 might not normally be necessary in view of its possible application in sewage treatment plants.

II. A. 3. Nitrogen Tetroxide

a. Incineration

Nitrogen tetroxide can be consumed in combustion with a hydrocarbon fuel, usually in the presence of air. Although a variety of large incinerators have been used in the past, at present this form of disposal invariably involves a flare burner in which propane and nitrogen tetroxide vapors mix at the exit plane of the burner and react; the burner is operated in a fuel rich mode and the atmospheric air surrounding the primary reaction zone apparently reacts with the excess fuel to prevent undesirable hydrocarbon emissions. These units have been installed in at least four facilities around the country.

b. Neutralization

The most common means of disposing is dilution followed by neutralization. The manufacturers recommend soda ash, lime, or other alkali for neutralization. Substances used by the organizations contacted also include sodium carbonate, triethanolamine, and sodium hydroxide. Several dilute and add the mixture to the same holding ponds used for hydrazines.

Vapors are sometimes treated in water-spray or baking soda scrubbers, or bubbled through water. The water effluent is sent to holding ponds to be neutralized as above.

c. Other Methods

Some waste N_2O_4 has been returned to the manufacturer. Vapors are often vented to atmosphere, sometimes with more or less elaborate precautions (as with the hydrazines.)

II. A. 4. Inhibited Red Fuming Nitric Acid

At the present time, there seems to be no significant IRFNA disposal activity in this country, although several organizations have had considerable past experience with IRFNA. Neutralization of IRFNA is essentially the same as neutralization of N_2O_4 , except that an additional step is necessary to precipitate the fluoride content. Disposal in a combustion reaction is also similar to the N_2O_4 case, except that the product gases might need to be treated by water scrubbing to avoid HF emissions. Except for the HF inhibitor, IRFNA disposal presents the same set of problems, albeit on a smaller scale, as those faced by the nitric acid industry.

The TRW study mentioned the possibilities of reaction with ammonium hydroxide to form an ammonium nitrate solution which can be used as a fertilizer, and steam distillation to yield concentrated acid.

B. PHASE 2

The purpose of Phase 2 was to evaluate the current disposal methods identified in Phase 1, on the basis of effectiveness in preventing the release of harmful constituents to the environment.

Tables I through IV on the following pages present, in summary form, our evaluation of the disposal techniques currently in use. We have assigned ratings as follows:

- A - Acceptable; no reservations
- B - Acceptable; slight reservations
- C - Acceptable; major reservations
- D - Not Acceptable except under very special circumstances
- F - Not Acceptable under any circumstance.

For hydrazines, both incineration and pond oxidation were given "A" ratings as means of disposing of the liquid phase. In addition, treatment with hydrogen peroxide was rated "B", and three other neutralization treatments were rated "C". The only generally acceptable current method of disposing

of hydrazine vapors is by scrubbing, which was rated "B". Scrubbing of course results in a liquid effluent that still must be disposed of by oxidation or neutralization.

Several neutralization reactions for liquid N_2O_4 were rated "B", as was simple water dilution. Incineration, a potentially good disposal method, has not been adequately demonstrated for liquid oxidizers, but flare burners were given an "A" rating for vapor disposal; vapor scrubbing was rated "B". All of the chemical treatments involve addition of other substances, in large quantity, that must also be disposed of ultimately. This secondary disposal problem is a significant disadvantage for these methods unless the products can be used as fertilizer rather than being discarded.

Disposal methods, and ratings, are essentially the same for IRFNA as for N_2O_4 , except that flare burners have not been designed for IRFNA to date (and this substance might represent a more difficult incineration problem), and a fluoride-precipitating agent is required in both the neutralization and simple dilution cases.

In dilute form, hydrogen peroxide is environmentally beneficial; decomposition, discharge to ponds or streams, and direct venting were all given "A" ratings.

These ratings were made on the basis of effectiveness of the disposal method and the environmental impact of the effluent. Other factors, such as worker safety and economic considerations, were taken into account where possible, but never as major factors. Quantitative rankings were considered, but not attempted since it was felt that true rankings are very application-dependent, and that any attempt on our part at ranking would tend to be misleading. For example, both incineration and oxidation ponds were given "A" ratings for disposal of liquid hydrazines. In any given application, one might be quite preferable to the other, but the choice would have to be made on the basis of a number of factors such as land availability, frequency of disposal and quantities, the nature of other activities taking place in the same area, etc. For the sake of this study, both are judged to be very effective and environmentally safe ways of disposing of liquid hydrazine; to

go farther and say one is generally preferable to the other would be to ignore the varying conditions and needs that might exist, and to do a disservice to future engineers who might have to justify use of the lower-rated system.

In cases where secondary disposal is required, the ratings are on the primary system only - that is, they assume the most efficacious means of secondary disposal will be used. This question arises primarily in connection with the formation of nitrates and nitrites from the neutralization of N_2O_4 or IRFNA. These nitrates and nitrites are in one sense a very valuable by-product, needed by the agricultural industry as fertilizers, but on the other hand they are environmentally quite hazardous if "dumped" into a river stream or lake, or even on land in any great concentration. Our ratings of "B" for most of these neutralization methods (and the related vapor scrubbing methods) are based on the assumption that these secondary products are put to good use as fertilizer, and spread over a very wide area, rather than discharged directly to flowing water or groundwater. Otherwise, ratings of "C" or "D" would apply.

TABLE I. OVERVIEW AND RATINGS - DISPOSAL OF N_2H_4 , MMH, UDMH AND AEROZINE 50

LIQUIDS				VAPORS			
Type of Treatment	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd	Comments
Incineration	A Acceptable for both large, small quantities	"SUE" unit, or comparable. Conventional large type units have undesirable start-up, maintenance, and aux. fuel consumption characteristics	None	Potentially acceptable, but unproven No rating given	The fact that hydrazine vapors are usually mixed with nitrogen or other waste gas is a problem.	Design Development Testing	Significant operational advantages over chemical neutralization. Dilute (H ₂ O) solutions are suitable for large conventional type units only
Open Pit Burning	D Unacceptable for routine disposal	Requires remote site, special precautions	None	Not applicable			Judged "generally acceptable" in TRW study and recommended by chemical industry.
Treatment with H ₂ O ₂	B Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			Possible problem with ammonia release
Treatment with Ca (ClO) ₂	C Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			Equivalent to Ca (ClO) ₂
Treatment with Na OCl	C Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			Equivalent to Ca (ClO) ₂
Treatment with HCl	Insufficient data - no rating given	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	Additional data needed if this method is to be seriously considered.	Not applicable			Recommended by manufacturer for MMH
Treatment with N ₂ O ₄	C Higher rating would apply if joint solution to two propellant disposal problems	-Dilution -Low rate -Careful control to avoid NO release	None	Insufficient data - no rating given.	Comparable to rocket thrust chamber	None (Not a promising method of disposal)	

TABLE I. OVERVIEW AND RATINGS - DISPOSAL OF N_2H_4 , MMH, UDMH AND AEROSINE 50

LIQUIDS				VAPORS			
Type of Treatment	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd	Comments
Incineration	A Acceptable for both large, small quantities	"SUE" unit, or comparable. Conventional large type units have undesirable start-up, maintenance, and aux. fuel consumption characteristics	None	Potentially acceptable, but unproven No rating given	The fact that hydrazine vapors are usually mixed with nitrogen or other ullage gas is a problem.	Design Development Testing	Significant operational advantages over chemical neutralization. Dilute (H ₂ O) solutions are suitable for large conventional type units only
Open Pit Burning	D Unacceptable for routine disposal	Requires remote site, special precautions	None	Not applicable			Judged "generally acceptable" in TRW Study and recommended by chemical industry.
Treatment with H ₂ O ₂	B Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			Possible problem with ammonia release
Treatment with Ca (ClO) ₂	C Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			
Treatment with NaOCl	C Acceptable subject to adequate means for secondary disposal	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	None	Not applicable			Equivalent to Ca (ClO) ₂
Treatment with HCl	Insufficient data - no rating given	-Dilution with H ₂ O req'd -Low rate because of heat release -Secondary disposal problem	Additional data needed if this method is to be seriously considered.	Not applicable			Recommended by manufacturer for MMH
Treatment with N ₂ O ₄	C Higher rating would apply if joint solution to two propellant disposal problems	-Dilution -Low rate -Careful control to avoid NO release	None	Insufficient data - no rating given.	Comparable to rocket thrust chamber	None (Not a promising method of disposal)	

TABLE I. OVERVIEW AND RATINGS - DISPOSAL OF N_2H_4 , MMH, UDMH AND AEROZINE 50 (Continued)

Type of Treatment	LIQUIDS				VAPORS			
	Overall Evaluation	Restrictions	Additional Work Req'd		Overall Evaluation	Restrictions	Additional Work Req'd	Comments
Dilution/Air Oxidation/Bacterial Action	<u>A</u> Acceptable for large or small quantities	Holding pond required Rate is slow Aeration (bubbling) and catalyst are desirable Ammonia is normally formed	None		Not applicable			If aeration and catalysts are not used, a stand-by system for rapidly neutralizing the hydrazine might be required in many applications.
Vapor Scrubbing	Not applicable				<u>B</u> Acceptable subject to remote gas discharge, suitable disposal of liquid discharge	Discharge liquor must be transferred to holding pond and treated by neutralization or air oxidation, as for diluted liquid hydrazines above		Only acceptable method for vapors (current) Vapors are normally received as one component in N_2 (or other ullage gas) mixture
Vent to Atmosphere	Not applicable (Evaporation is not acceptable except for very small quantities)				<u>D</u> Unacceptable for future application except under special circumstances			An upper limit of 0.01 ppm hydrazine in atmospheric air is proposed in the TRW Study
Open Burning	<u>F</u> Unacceptable - Uncontrolled atmospheric discharge				<u>F</u> Unacceptable			Differs from open pit burning in that no special equipment is used
Ocean Dumping	<u>F</u> Unacceptable due to future legal restriction				Not applicable			
Pouring on Ground	<u>D</u> Acceptable only for very small quantities	-Remote area, adequate dispersal -Quantities greater than 250 ml or so might cause safety or environmental problems			Not applicable			Very desirable method for very small quantities

TABLE II. OVERVIEW AND RATINGS - DISPOSAL OF N_2O_4

Type of Treatment	LIQUIDS			VAPORS			Comments
	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd	
Incineration	Potentially acceptable, but not adequately demonstrated. Note - that liquids can be evaporated readily and incinerated as vapors No rating given		-Additional development and testing of "SUE" incinerator as an oxidizer disposal unit -Flare Burner could be used in conjunction with evaporation chamber, requiring design, development & test.	A Acceptable for large and small quantities	-Needs liquid-vapor separator -Flare burner only is acceptable at present	Development, testing of "SUE" or comparable closed incinerators	
Neutralization with Na_2CO_3	B Acceptable subject to adequate means for secondary disposal	-Dilution with copious water required -Low rate because of heat generation -Effluent may be toxic and corrosive, and requires ultimate ground disposal	None	Not applicable - but see vapor scrubbing below			
Neutralization with NaOH	B- Acceptable subject to adequate means for secondary disposal - strong base presents safety problem	Same as above	None	Same as above			
Neutralization with $NaHCO_3$	B Acceptable subject to adequate means for secondary disposal	Same as above	None	Same as above			

TABLE II. OVERVIEW AND RATINGS - DISPOSAL OF N_2O_4

Type of Treatment	LIQUIDS			VAPORS			Comments
	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd	
Incineration	Potentially acceptable, but not adequately demonstrated. Note - that liquids can be evaporated readily and incinerated as vapors No rating given		-Additional development and testing of "SUE" incinerator as an oxidizer disposal unit -Flare Burner could be used in conjunction with evaporation chamber, requiring design, development & test.	A Acceptable for large and small quantities	-Needs liquid-vapor separator -Flare burner only is acceptable at present	Development, testing of "SUE" or comparable closed incinerators	
Neutralization with Na_2CO_3	B Acceptable subject to adequate means for secondary disposal	-Dilution with copious water required -Low rate because of heat generation -Effluent may be toxic and corrosive, and requires ultimate ground disposal	None	Not applicable - but see vapor scrubbing below			
Neutralization with NaOH	B Acceptable subject to adequate means for secondary disposal - strong base presents safety problem	Same as above	None	Same as above			
Neutralization with $NaHCO_3$	B Acceptable subject to adequate means for secondary disposal	Same as above	None	Same as above			

TABLE II. OVERVIEW AND RATINGS - DISPOSAL OF N_2O_4 (Continued)

Type of Treatment	LIQUIDS			VAPORS		
	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd
Neutralization with $Ca(OH)_2$	<u>C</u> Strong base; more of an environmental problem than preceding methods	Same as above	None	Same as above		
Neutralization with $Mg(OH)_2$	<u>C</u> Similar to $Ca(OH)_2$	Same as above	None	Same as above		Higher chemical cost than preceding methods
Neutralization with Triethanolamine	Insufficient data; no rating given			Not applicable		Use discontinued due to explosion (only used by one organization)
Vapor scrubbing - absorption in water	No: applicable			<u>B</u> Acceptable for large or small quantities, subject to remote vapor discharge, suitable disposal of liquid discharge	Requires further treatment of liquor - neutralization as above, or dilution	None
Vapor scrubbing - absorption in $NaHCO_3$	Not applicable			<u>B</u> Acceptable subject to remote vapor discharge, suitable disposal of liquid discharge	No further treatment required, but liquor is highly corrosive (solution of sodium salts) & might present other disposal problems	None
Atmospheric venting	Not applicable			<u>D</u> Unacceptable except for small quantities, low rates		NO_2 , NO emissions
Simple water dilution	<u>B</u> Subject to availability of sufficient water			Not applicable		Preferable to neutralization in terms of absence of secondary disposal problem

TABLE III. OVERVIEW AND RATINGS - DISPOSAL OF IRFNA

LIQUIDS				VAPORS			
Type of Treatment	Overall Evaluation	Restrictions	Additional Work Req'd	Overall Evaluation	Restrictions	Additional Work Req'd	Comments
Incineration	Not adequately demonstrated - no rating given	HF presents special problems	Additional development & testing of "SUE" or comparable incinerators	Not adequately demonstrated, no rating given	HF presents special problems	Additional development & testing of flare burner and/or SUE comparable incinerators	Vapors are likely to be mixture of N_2 , NO_2 , HNO_3 , HF , and NO
Treatment with Na_2CO_3 and $Ca(OH)_2$	B Acceptable subject to adequate means for secondary disposal	-Residual CaF_2 will remain (50 - 100 ppm) -Effluent is toxic and corrosive -Copious dilution of effluent is required	None	Not applicable - but see vapor scrubbing below			Fluoride-precipitating agent might be dispensed with $[Ca(OH)_2]$
Treatment with $NaOH$ and $Ca(OH)_2$	B Similar to above, but stronger base presents safety problem	Same as above	None	Not applicable - (see vapor scrubbing)			Same as above
Treatment with NH_4OH and $Ca(OH)_2$	B Similar to above	Same as above	None	Not applicable - (see vapor scrubbing)			Same as above Ammonia odor
Simple water dilution	B Acceptable for large or small quantities, subject to availability of sufficient water	Might require $Ca(OH)_2$ to precipitate fluoride	None	Same as above			Preferable to neutralization in terms of NO_x emissions
Vapor scrubbing- with water	Not applicable			B Acceptable	Same as for "simple water dilution" of liquid	None	Same as above
Vapor scrubbing- with $NaHCO_3$	Not applicable			B Acceptable subject to remote vapor discharge, suitable disposal of liquid discharge	Same as for vapor scrubbing ($NaHCO_3$) of N_2O_4 vapors	None	Same as for vapor scrubbing ($NaHCO_3$) of N_2O_4 Same scrubber system could be used for N_2O_4 , IRFNA
Atmospheric venting	Not applicable			D Unacceptable except in very small quantities			

TABLE IV. DISPOSAL OF HYDROGEN PEROXIDE

Type of Treatment	LIQUIDS				VAPORS				Comments
	Overall Evaluation	Restrictions	Additional Work Req'd		Overall Evaluation	Restrictions	Additional Work Req'd		
Decomposition	A Acceptable in small or large quantities		None		Not applicable				Catalyst could be used, but not required - (heat also)
Biological (discharge to pond or stream)	A Acceptable in all quantities	Pre-dilution required to prevent strong reaction with organic material or harm to aquatic life	None		Not applicable				Beneficial effect on environment
Pouring on Ground	B Acceptable in small quantities		None		Not applicable				
Vent to Atmosphere	Not applicable				A Acceptable for any quantities	No special restrictions	None		Vapors are not toxic, but cause discomfort (eyes and nose) in case of direct exposure No adverse environmental effects

C. PHASE 3

The purpose of Phase 3 was to investigate new alternative concepts for propellant disposal, and to perform additional studies related to the application of various disposal concepts.

Several new alternative concepts were studied, both experimentally and theoretically. Especially favorable results were obtained in the cases of vapor condensation and gamma irradiation. Direct vapor phase addition of N_2O_4 to holding ponds was successfully accomplished using porous plate spargers; if the vapor pumping requirements are not prohibitive this method might be a viable alternative to the use of a scrubber in some applications. Insoluble calcium carbonate was shown to have distinct advantages as a neutralizing agent for N_2O_4 relative to the commonly used water soluble reagents. Catalytic decomposition offers several promising possibilities, but development and evaluation will require a relatively major research program. It was found, however, that common copper sulfate and iron oxide catalysts are extremely beneficial when used in conjunction with aeration. Ozone oxidation was quite successful, but might not be justified relative to air oxidation.

The application studies were basically of two types: those treating the application of particular disposal methods, and those treating the application of various disposal methods to specific disposal situations. In the former category, primary attention was given to aeration and to fuel-oxidizer reactions in dilute solutions, including laboratory work as well as theoretical considerations. In addition, scrubber design criteria were studied, and an experimental evaluation of the removal of fluoride from dilute IRFNA solutions was performed. The second category of application studies included waste handling and facility location considerations, fume hood design criteria, and a discussion of propellant disposal at contingency landing sites.

Tables V, VI, and VII on the following pages present the results of this phase of the study in summary form. Details are presented in the final two sections of this report, which deal with "Alternative Disposal Concepts" and "Application Studies", respectively.

TABLE V. NEW METHODS

Description	Nature of Investigation	Liquid	Preliminary Evaluation	Vapor
1. Vapor Condensation - Removal of vapors from vent gas by cooling.	Theoretical Numerical for 3 atm, 300°K, N_2H_4 , MMH, UDMH, N_2O_4 Experimental for MMH	Not applicable	Hydrazines and N_2O_4 : "A". Economics seem extremely favorable. Conceptual design and development phases are justified. Possibility of condensing N_2O_4 from IRFNA has not been studied.	
1a. Vapor condensation combined with steam scrubbing.	Experimental for MMH	Not applicable	MMH: "A". Others not evaluated, but would be at least as good as simple recondensation in all cases.	
2. Gamma irradiation of aqueous mixtures	Experimental for aqueous solutions of N_2H_4 , MMH, and N_2O_4	Hydrazines: "A". N_2O_4 : "D" (decomposes to form NO_x). Conceptual design and development phases are justified	Not applicable except as secondary treatment for scrubber discharge liquid.	
3. Catalytic decomposition (not including the use of catalysts in conjunction with aeration, evaluated elsewhere)	Inquiries to manufacturers regarding all listed propellants	Hydrazines and H_2O_2 : potential "A". IRFNA: probably not feasible because of halogen content. N_2O_4 : unknown. Further study required for thorough evaluation.	Hydrazines, N_2O_2 and N_2O_4 : potential "A". IRFNA: probably not feasible because of halogen content. Further study required for thorough evaluation.	
4. Calcium carbonate as a neutralization agent for dilute solutions of N_2O_4 and IRFNA	Experimental for N_2O_4 liquid and vapor	N_2O_4 and IRFNA: "A". Others: not applicable. End product can be spread on ground as fertilizer; should not be added directly to rivers, ocean, etc.	N_2O_4 and IRFNA: "A". Others: not applicable. Extremely small bubbles are required.	
5. Vapor phase addition of N_2O_4 to holding ponds	Experimental, with and without calcium carbonate (limestone) chips	Not applicable	Rating depends on eventual disposal methods (neutralization with limestone or hydrazine fuels). Feasibility of vapor phase addition has been established, subject to the formation of very small bubbles.	
6. Oxidation of diluted hydrazine fuels by ozone bubbling	Experimental for N_2H_4	"A". Extremely effective and fast. Trade-offs between ozone and air bubbling should be carefully considered for each application	Not applicable	



TABLE VI. APPLICATION STUDIES ON EXISTING DISPOSAL METHODS

Disposal Method	Nature of Investigation	Major Conclusions or Other Results
1. Fuel-oxidizer reactions in dilute solutions	<p>a. Calculations of energy balance and temperature rise; transient temperature rise due to sudden fuel/oxidizer addition, and steady state temperature rise due to steady fuel/oxidizer flow.</p> <p>b. Experimental measurements of peak temperature rise resulting from mixing of N_2H_4 and MMH with N_2O_4, IRFNA, and acetic acid; and urea with N_2O_4 and IRFNA.</p> <p>c. Experimental investigation of the neutralization of 5% hydrazine solutions using vapor phase nitrogen tetroxide.</p>	<p>Established basis for determining minimum size for reaction ponds. Demonstrated that thermal problems are not serious for "normal" sized ponds at atmospheric temperatures receiving "normal" amounts of propellants, but do become restrictive when steady state is reached.</p> <p>Concentrations up to 5% can be mixed with no more than 12°C temperature rise. Temperature rise when urea is used in place of the fuel, or acetic acid in place of the nitrogen-based oxidizers, is minimal.</p>
2. Aeration ponds for hydrazine (with or without catalysts)	<p>a. Visits to existing aeration ponds and receipt of data from JSC and WTR.</p> <p>b. Experimental investigations of air bubbling in five gallon batches of diluted (925 ppm) MMH and N_2H_4, with and without $CuSO_4$ and/or Fe_2O_3 catalysts.</p> <p>c. Theoretical considerations of bubble growth, detachment, and rise.</p>	<p>Reaction was successful, with 11°C temperature rise and neutralization to pH 7.2. No NO_2 gas was seen to escape.</p> <p>Rapid oxidation is achieved once dissolved oxygen reaches saturation level. Dissolved oxygen seems to rise much more rapidly with air bubbling than with spray. Neither method appears to result in significant atmospheric release of hydrazine.</p> <p>Rapid decomposition of either hydrazine is possible. Use of a catalyst is very beneficial in achieving rapid decomposition. An aeration pond with catalyst is probably the best of existing disposal methods for liquid hydrazines for most applications.</p> <p>Equations and graphs for calculating bubble size for any aerator, including consideration of corrections for high flow rate and closely-spaced bubbles. Means of achieving very small bubbles. Advantage of large or small bubbles. Equations and graphs for bubble rise velocity.</p> <p>Charts and graphs, literature references.</p>
3. Scrubbers	<p>Theoretical considerations on flow rates and sizing of scrubbers, with especial reference to counter-current scrubbers.</p>	
4. Precipitation of fluoride from diluted IRFNA solution.	<p>Experiments on precipitation from a solution containing 200 ppm fluoride, 2.0 to 2.6% nitrate, using $CaCl_2$ and $Ca(OH)_2$.</p>	<p>Fluoride could only be reduced to 80 ppm (best run) to 150 ppm (worst run). Later results indicate that $Ca_3(PO_4)_2$ is much more effective.</p>



TABLE VII. APPLICATION STUDIES ON DISPOSAL PROBLEMS

Disposal Situation	Nature of Study
1. Parts handling fume hoods	Design considerations - evaporation rates, flow rates, sizes. Use of air mixing sections or scrubbers.
2. Dumping of propellants from drum type containers.	Consideration of commercially - available, remote-control equipment.
3. Launch site	Consideration and discussion of alternatives. Recommended pond location.
4. Orbiter processing facility	Scrubber size and flow rate recommendations, and recommended pond location.
5. Hypergolic maintenance facility	Number, size, and flow rates for fume hoods with scrubbers. Recommended pond location.
6. End of runway	Recommended pond or tank location for emergency use.
7. Contingency landing sites	Comparison of disposal methods, and discussion. It is our conclusion that a requirement exists for the design and development of an air transportable holding (reaction) pond.
8. Transportation of hypergolic wastes from collection to disposal sites	Preliminary cost estimates for various alternatives.

III. RECOMMENDATIONS FOR FURTHER STUDY

A number of areas have been identified in this study where further effort is believed to be justified by the possibility of significant advances in waste propellant disposal technology. These areas are listed below:

1. Vapor condensation. The greatest need, in terms of new disposal methods, identified in this study is an alternative to water scrubbing/liquid effluent treatment for hydrazine vapors. Analyses and experiments indicated that recondensation looks very promising from both the environmental and economic points of view. Continuation to design and development phases seems well justified. The method has the added advantage of being even more promising in the case of N_2O_4 vapors, where the best current method, the flare burner, requires a dependable supply of propane or other fuel and might have other disadvantages: we have learned that the most recent and extensive installation, at Johnson Space Center, was decommissioned almost immediately after becoming operational.
2. Catalytic decomposition. Another method that might be promising for disposal of hydrazine vapors is direct catalytic decomposition. A feasibility study is probably the next step here.
3. Holding ponds. A number of holding pond-related disposal techniques are either in use, or have been investigated in this study. The next step is to consider in detail the overall design of a holding pond to receive both fuels and oxidizers, in varying amounts, making the best use of aerators, circulation pumps, calcium carbonate layers, gamma irradiation or ozone generation if necessary, and chemical neutralization if necessary. Other considerations are the need for an impervious liner to prevent seepage into the ground, the need for wildlife protection (fences and perhaps some sort of dome) and provisions for proper monitoring and control.
4. Combustion. Combustion devices identified in this study as being desirable for certain propellant disposal problems have not been adapted or tested for other propellants. The flare burner could probably be developed for other oxidizer vapors besides N_2O_4 , and

possibly for fuel vapors as well. The SUE incinerator could perhaps be modified for destruction of nitrogen-fuel vapor mixtures, and another attempt could be made to apply this unit for oxidizer disposal. This design could also probably be carried to a higher stage of development with advances in nozzle design, secondary air injection, etc., that would incorporate recently-developed combustor technology from the gas turbine field.

5. Contingency landing sites. The design of an air transportable holding pond--perhaps a number of modules that could be assembled on-site to any required size--appears to offer the best solution to the problem of propellant disposal at contingency landing sites. One problem is selection of the best liner material. A combination of combustion devices and scrubbers that could be flown to the point of need could also be designed for this purpose, although this disposal approach is dependent on the availability of a fairly large supply of auxiliary fuel at each landing site. If one of these two approaches is not adopted, disposal will probably have to rely on the possibility of excavating a holding pond on the spot at the time of need.

THE CURRENT STATE OF THE ART (PHASE 1)

	Page
I. The Organizations Contacted	25
A. The Compilation Procedure	25
B. Response to Inquiries	30
II. Results of the Literature Survey	32
A. Primary Bibliography	34
B. Secondary Bibliography	36
III. Disposal Methods Recommended by the Chemical Industry	37
IV. Disposal Recommendations from the TRW Study	42
V. Current Disposal Practices	15
A. Hydrazine - General	46
B. Anhydrous Hydrazine	50
C. Monomethyl Hydrazine	50
D. Hydrogen Peroxide	51
E. Nitrogen Tetroxide	51
F. Inhibited Red Fuming Nitric Acid	53
G. Disposal at the Eastern and Western Test Ranges	54
H. Commercial Manufacture of Nitric Acid	56
VI. Special Equipment and Other Solutions	57

I. THE ORGANIZATIONS CONTACTED

A. THE COMPILATION PROCEDURE

We first compiled an extensive list of both manufacturers and users of the specified propellants from sources including Thomas Register, World Aviation Directory, Aviation Week's "Forecast and Inventory" issue of 19 May 1973, miscellaneous library sources, personal contacts, and suggestions made by NASA's technical review team. We included several foreign organizations in the belief that it was possible that their approaches might be substantially different from those in this country. Every effort was made to make the list as comprehensive as possible, with the assumption that we would elicit negative responses from many of the organizations - especially some of the smaller chemical companies.

On the basis of what we knew of their activities, the initial list was divided as follows (with some organizations involved with more than one propellant):

Hydrazines (all varieties):	43
MMH:	8
UDMH:	8
Aerozine 50:	9
Hydrogen Peroxide:	16
Nitrogen Tetroxide:	15
IRFNA:	7
Catalysts:	3

In the interest of completeness the list also included disposal equipment manufacturers from Thomas Register and pollution control and chemical engineering journals. The fourteen chosen certainly did not constitute an exhaustive list but, rather, represented organizations we believed most likely to have been exposed to the problem of disposing of hypergolic propellants. Several were subsidiaries of companies listed as users or manufacturers.

Altogether, seventy nine organizations were contacted at the beginning of the study, thirty five of which were chemical companies. The foreign companies and organizations were based in the following countries:

France:	5
Germany:	4
Britain:	2
Japan:	4
Sweden:	2
Spain	1

Eventually, the total number of contacts (and attempted contacts) reached ninety two as a result of suggestions from people contacted initially and other additions. A complete list of these organizations follows. This list does not include companies contacted during Phase 3 in connection with our effort to evaluate the potential for catalytic decomposition as a disposal method.

1. Positive Replies - Techniques

Aerojet Liquid Rocket Co., Sacramento, California
Allied Chemical Corp., Solvay, New York
Battelle Columbus Laboratories, Columbus, Ohio
Bell Aerospace Co., Buffalo, New York
E. I. DuPont de Nemours & Co., Wilmington, Delaware
Engelhard Minerals & Chemical Corp., East Newark, New Jersey
Fisons Limited, Cambridge, England
FMC Corp., Environmental Equipment Div., Chicago, Illinois
FMC Corp., Industrial Chemical Div., New York, New York
Hercules Inc., Wilmington, Delaware
Marquardt Co., Van Nuys, California
Martin-Marietta Aerospace, Cape Canaveral, Florida
Martin-Marietta Aerospace, Denver Div., Denver, Colorado
Martin-Marietta Aerospace, Vandenburg AFB, California
McDonnell Douglas Astronautics Co., Cape Canaveral, Florida
McDonnell Douglas Astronautics Co., Huntington Beach, California
NASA - Johnson Space Center
NASA - Western Test Range
NASA - White Sands, New Mexico

Olin Chemicals, Stamford, Connecticut
Pan American World Airways, Cape Canaveral, Florida
PPG Industries, Inc., Pittsburgh, Pennsylvania
Rockwell International, Cape Canaveral, Florida
Rockwell International, Space Div., Downey, California
SAAB - Scania, Linköping, Sweden
Shell Development Co., Houston, Texas
Sundstrand Aviation, Rockford, Illinois
Thermal Research & Engineering Corp., Conshohocken, Pennsylvania
Tri-Mer Corp., Owosso, Michigan
TRW Systems, Redondo Beach, California
United Aircraft, Hamilton Standard Div., Windsor Locks, Connecticut
United Aircraft, United Technology Center, Sunnyvale, California
USAF Eastern Test Range, Cape Canaveral, Florida
USAF Western Test Range, Vandenberg AFB, California
Walter Kidde & Co., Inc., Belleville, New Jersey

2. Positive Replies - Suggestions

Battelle Pacific Northwest Laboratory, Richland, Washington
Boeing Aerospace Co., Seattle, Washington
Fairmount Chemical Co., Inc., Newark, New Jersey
Lockheed Missiles & Space Company Inc., Sunnyvale, California
Rockwell International, Rocketdyne Div., Canoga Park, California

3. Negative Replies

A and S Corp., Verona, New Jersey
Alloychem Inc., New York, New York
American Chemical & Refining Co., Inc., Waterbury, Connecticut
Chemec Process Systems, Inc., Tappan, New York
Dow Chemical Co., Midland, Michigan
Envirogenics Systems Co., El Monte, California
European Aerospace Corp., Greenwich, Connecticut
FECO, Cleveland, Ohio

Hawker Siddeley Dynamics Ltd., Hatfield, Herts., England
 ICN - K & K Laboratories, Plainview, New York
 Industrial Chemical and Dye Corp., New York, New York
 Instel Corp., New York, New York
 Joy Manufacturing Co., Denver Equip. Div., Denver, Colorado
 Kuehne Chemical Co., Elizabeth, New Jersey
 Mallinckrodt Chemical Works, St. Louis, Missouri
 McKesson Chemical Co., New York, New York
 National Distillers and Chemical Corp., U. S. Industrial Chemical Co.
 Div., New York, New York
 National Polychemicals, Inc., Wilmington, Massachusetts
 Seymour Mfg. Co., Seymour, Indiana
 Space General Co., El Monte, California
 Universal Oil Products Co., Des Plaines, Illinois
 Volvo Flygmotor Ab., Trollhattan, Sweden
 Westinghouse Electric Corp., Infilco Div., Richmond, Virginia

4. No Reply

City Chemical Corp., New York, New York
 Combustion Engineering Inc., Chicago, Illinois
 Environment One Corp., Schenectady, New York
 Erno Raumfahrttechnik GMBH, Bremen, West Germany
 Farbenfabriken Bayer A.G., Leverkusen, West Germany
 Hikari Chemical Industries Co., Ltd., Ohmiya City, Japan
 Japan Hydrazine Co., Tokyo, Japan
 Jones Chemicals, Inc., Caledonia, New York
 Kraft Chemical Co., Chicago, Illinois
 Messerschmitt - Boelkow - Blohm GMBH, Munich, West Germany
 Mitsubishi Heavy Industries, Ltd., Tokyo, Japan
 Monopole des Poudres, Toulouse, France
 Mutchler Chemical Co., Inc., New York, New York
 Office National D'eludes et de Recherches Aerospatiales, Chatillon, France

Otsuka Chemical Co., Osaka, Japan
Pennsalt Chemicals Corp., Philadelphia, Pennsylvania
Rocket Research Corp., Redmond, Washington
Shepard Chemical Industries, Inc., New York, New York
Societe des Produits Doazotes, Lannemezan, France
Societe Europeene de Propulsion, Puteaux, France
Technologieforschung GMBH, Stuttgart, West Germany
TRW, Inc., Environmental Services, Redondo Beach, California
Uniroyal, Inc., Naugatuck, Connecticut

5. Not Deliverable

Astroage Corp., Buffalo, New York
E. R. Squibb and Sons, New York, New York
Ogden Technology Labs, Inc., Farmingdale, New York
Quimica Sintetica, Madrid, Spain
Seaway Chemical Corp., Buffalo, New York
Whiteley Hydraulics, Inc., Melrose, Massachusetts

B. THE RESPONSE

Table VIII presents an overview of the response detailed at the end of the preceding section. "Positive" means a meaningful input to our study; "negative" means a response to the effect that the firm is not concerned with the listed propellants; "zero" means no response.

TABLE VIII
CONTACTS AND RESPONSES BY CATEGORY

Category	Response				
	Positive		Negative	Zero	
	Techniques	Suggestions		No Response	Letter Return
Chemical Manufacturers	9	1	9	13	5
Users	23	4	5	7	1
Equipment Manufacturers	4	0	9	3	0
Totals	35	5	23	23	6

Only one American firm actually known to be using hypergolic propellants is included in the "zero" category, and that only after repeated attempts to gain their cooperation. Others in this category are firms that have gone out of business, some that were considered remote possibilities, most of the overseas organizations we attempted to contact, etc. One thing learned in performing this study is that many "chemical companies" don't actually manufacture chemicals. As we had anticipated, many of the smaller chemical companies did not respond at all.

One surprise was that interest is so low among manufacturers of chemical disposal equipment. However, we found that some aerospace companies are aware of the difficulties in disposing of these materials, and of the potential market for devices to accomplish this within present environmental limitations.

II. RESULTS OF THE LITERATURE SURVEY

The literature survey began with a computer search performed by the KSC Library, which tried all reasonable pairings of the terms "propellant", "fuel", and "oxidizer", as well as the seven specific propellant names, with "disposal", "waste", and "pollution", searching back to 1966. No papers or reports were found by this method. Further work, questions to people in industry, etc., turned up a few papers and reports, as listed below under "Primary Bibliography."

In addition to these reports, there are also a large number of manuals and reports from the early 1960's on the handling of these propellants. These manuals are adequately referenced by the various technical bulletins listed below, and are not included in this list; the current availability of many of them is uncertain, they are not primarily concerned with disposal, and of course they do not help in ascertaining current disposal practice. Also of interest are the sections in chemical and aerospace encyclopedias, etc., dealing with the substances of interest to this study.

The article by Chase is an early description of the incinerator built at Cape Canaveral by Thermal Research and Engineering Corp. in connection with the Titan II program. The Conner and Gebhart report describes disposal practices at the Bell Aerospace facility. Haskins' article is a very recent description of Du Pont's work with hydrogen peroxide as an oxygen source for the treatment of sewage in existing plants. The report by Ottinger et al is the result of a very large study by TRW of disposal techniques for hundreds of different hazardous materials. The Hutson report covers work done under contract to the Air Force on the performance of the "SUE" incinerator as a means of disposing of hydrazines and N_2O_4 . The Smith report covers testing of a flare burner at White Sands. The papers by Astor et al, Giaque and Kemp, and Scott et al, all represent early, basic work on the thermodynamic properties of hypergolic propellants, while the Fan and Mason paper is a more recent, detailed look at the properties of equilibrium N_2O_4 - NO_2 mixtures. Other papers on the properties of these propellants can be found via the Index volumes of Chemical Abstracts, with the period 1948-1963 being especially fruitful.

In addition to these reports, a number of other papers that are of some interest for this study, but not directly related to propellant disposal, are included below as a "Secondary Bibliography". This list is of course not comprehensive, as the region of interest is essentially unbounded, but are included to simply give an entry point into some of the literature on aspects of the chemistry of these propellants that might be important to disposal considerations.

It should also be mentioned that there exists a very large and growing literature on the formation, effects, prevention, and removal of oxides of nitrogen in atmospheric discharges. This literature is of interest in connection with the disposal of either of the nitrogen-based oxidizers and also with combustion - based disposal of hypergolic fuels.

A. Primary Bibliography

- J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, "The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures, Entropy, and Thermodynamic Functions of Methylhydrazine." J. Am. Chem. Soc., Vol. 73, 1939-43 (1951).
- J. G. Aston, J. L. Wood and T. P. Zolki, "The Thermodynamic Properties and Configuration of Unsymmetrical Dimethylhydrazine." J. Am. Chem. Soc., Vol. 75, 6202-04 (1953).
- C. E. Chase, "Automated Missile Waste Disposal". Instrumentation, Vol. 15, No. 3 (Minneapolis-Honeywell Regulator Co., Industrial Products Group, Philadelphia, Pa.)
- W. J. Conner and H. W. Gebhart, "Pollutants and Pollution Control for the Agena Rocket Engine". AIAA Paper No. 71-716, presented at the 7th Propulsion Joint Specialist Conference, Salt Lake City, June 14-18, 1971.
- S. S. T. Fan and D. M. Mason, "Properties of the System $N_2O_4 = 2NO_2 = 2NO + O_2$." Journal of Chemical and Engineering Data, Vol. 7, pp. 183-186 (1962).
- W. F. Giauque and J. D. Kemp, "The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $N_2O_4 = 2NO_2 = 2NO + O_2$." J. Chem. Phys., Vol. 6, pp. 40-52 (1938).
- James W. Haskins, Jr., " H_2O_2 Looks Good for Sewage Treatment". Innovation, Fall 1973, pp. 6-9 (E. I. Du Pont de Nemours & Co., Inc., Wilmington, Delaware 19898).
- Joel E. Hutson, "Toxic Waste Burner Evaluation." Final Report, AFRPL Contract No. F04611-73-C-0007 (Marquardt Company Report S-1271), November 1973.
- R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy, and C. C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste". Report No. 21485-6013-RU-00, TRW Systems Group, 1 February 1973, Prepared for Environmental Protection Agency, Contract No. 68-03-0089. (See especially Vols. I, XII).
- D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, "Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions." J. Am. Chem. Soc., Vol. 71, 2293-97 (1949).

Irwin D. Smith, Nitrogen Tetroxide Disposal Unit Combustion Products.
NASA TN D-3965, May 1967.

"Anhydrous Hydrazine Handling & Storage." Olin Chemicals, 745 Fifth Ave.,
New York, New York. 10022.

"Chemical Safety Data Sheet SD-5, Properties and Essential Information for
Safe Handling and Use of Nitric Acid." Manufacturing Chemists'
Association, 1825 Connecticut Ave., N. W., Washington, D. C. 20009,
1961.

"Chemical Safety Data Sheet SD-53, Properties and Essential Information for
Safe Handling and Use of Hydrogen Peroxide." Manufacturing Chemists'
Association, 1825 Connecticut Ave., N. W., Washington, D. C. 20009,
1969.

"Concentrated Hydrogen Peroxide." Bulletin No. 46, FMC Corp., Inorganic
Chemicals Div., 633 Third Ave., New York, New York, 10017.

"Dimazine: Unsymmetrical Dimethylhydrazine." FMC Corp., Organic
Chemicals Div., 633 Third Ave., New York, New York 10017.

"Hercules Nitrogen Tetroxide." Product Data No. 2004, Synthetics Dept.,
Hercules Ave., Wilmington, Delaware.

"Liquid Propellant Handling, Storage and Transportation." Volume III of
Chemical Rocket/Propellant Hazards, by the Liquid Propellant Handling
and Storage Committee of the JANNAF Hazards Working Group.
CPIA Publication No. 194, AD 870259, May 1972.

"Material Safety Data Sheet: Hydrogen Peroxide 90%." FMC Corp., 1710
South Agness Road, Box 1056, Vancouver, Washington 98660.

"Material Safety Data Sheet SOS-4: Nitric Acid." Synthetics Department,
Hercules Inc., Wilmington, Delaware 19899.

"Material Safety Data Sheet SOS-26: Nitrogen Tetroxide." Synthetics
Department, Hercules Inc., Wilmington, Delaware 19899.

"Material Safety Data Sheet: Unsymmetrical Dimethyl Hydrazine." FMC
Corp., 1701 Patapsco Avenue, Baltimore, Maryland 21226.

"Monomethyl Hydrazine Handling and Storage." Olin Corp. Chemicals Div.,
120 Long Ridge Road, Stamford, Connecticut 06904.

"Precautions and Handling Procedures for Hercules Nitrogen Tetroxide
(N_2O_4)." Bulletin SI-111, Synthetics Department, Hercules Inc.,
Wilmington, Delaware 19899.

"Treatment of Waste Containing Hydrogen Peroxide, Hydrazine, and Methanol."
Chemistry and Industry, 1951, pages 1104-6.

B. Secondary Bibliography

- Anon., "Nitric Acid Producers Ponder New Technology." Chemical Engineering, December 15, 1969, p. 50.
- Anon., "Nitric Acid Rolls On." Chemical Engineering, June 29, 1970, pp. 24-25.
- D. S. Burgess, G. H. Martindill, J. N. Murphy, F. J. Perzak, J. M. Singer, and R. W. Van Dolah, "Inerting and Extinguishment of Aerozine-50 with Water and/or CF_3Br ." J. Spacecraft, Vol. 6, 1969, pp. 1259-1268.
- Seymour Calvert, "Source Control by Liquid Scrubbing." Ch. 46 in Air Pollution, Vol. III, ed. by Arthur Stern, Academic Press, New York, 1968.
- Theodore Christos, Yael Miron, Harry James and Henry Perlec, "Combustion Characteristics of Condensed-Phase Hydrazine-Type Fuels with Nitrogen Tetroxide". J. Spacecraft, Vol. 4, 1967, pp. 1224-1229.
- G. R. Gillespie, A. A. Boyum and M. F. Collins, "Catalytic Purification of Nitric Acid Tail Gas: A New Approach." Presented at the AIChE Annual Meeting, San Francisco, December 2, 1971.
- H. Greer, "Vacuum Starting of Reactors for Catalytic Decomposition of Hydrazine." J. Spacecraft, Vol. 7, 1970, pp. 522-528.
- H. Greer, S. M. King, P. C. Marks, and D. Taylor, "Experimental Evaluation of Catalysts for Monopropellant Hydrazine Propulsion." J. Spacecraft, Vol. 8, 1971, pp. 105-110.
- M. H. Heinz and G. F. Orton, "Effects of Sterilization and Decontamination on Hydrazine Propulsion Systems." J. Spacecraft, Vol. 6, 1969, pp. 853-855.
- Frend J. Miner and Paul G. Hagan, "Rate of Hydrogen Peroxide Decomposition in Nitric Acid Solutions." Ind. Eng. Chem. Process Design and Development, Vol. 11, 1972, pp. 547-549.
- D. J. Newman, "Nitric Acid Plant Pollutants." Chemical Engineering Progress, Vol. 67, 1971, pp. 79-84.
- Michel A. Saad and Michael B. Detweiler, "Analysis of N_2H_4 - RFNA Reaction Product." AIAA Journal, Vol. 7, 1969, pp. 1588-1592.
- Michel A. Saad, Michael B. Detweiler, and Michael A. Sweeney, "Analysis of Reaction Products of Nitrogen Tetroxide with Hydrazines under Non-ignition Conditions." AIAA Journal, Vol. 10, 1972, pp. 1073-1078.
- Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition. Interscience Publishers, New York 1966.

III. DISPOSAL METHODS RECOMMENDED BY THE CHEMICAL INDUSTRY

These methods are taken from the technical bulletins and data sheets listed in the Literature Survey, Section II above.

1. Anhydrous Hydrazine (Source of information: Olin Chemicals)

"Waste hydrazine from spills or process effluent presents a problem of neutralization prior to sewerage. Commercial calcium hypochlorite, containing 70% available chlorine (HTH), provides an ideal solution to this problem. The reaction between the hydrazine and calcium hypochlorite yields nitrogen and calcium chloride. Other decontaminants may also be used (see Table IX).

"Drains from areas of hydrazine handling should lead to a sump or holding pond where neutralization can be effected in a very dilute solution. One mole of calcium hypochlorite is required per mole of hydrazine. On a weight basis this is equivalent to 6.4 pounds of HTH per pound of hydrazine. Recommended usage is seven to ten pounds of HTH per pound of hydrazine to provide an excess of HTH. This is roughly equivalent to 0.6 to 1.0 per pound of HTH per gallon of 1% solution of hydrazine.

"Neutralization of hydrazine with HTH is complete and rapid at pH 5.0 to 8.0. At lower pH, the reaction is complete, but may require a longer period of time. At higher pH, the reaction may not proceed to completion.

"A dilute solution of hydrogen peroxide may also be used to neutralize dilute hydrazine wastes. One mole of hydrogen peroxide is required per mole of hydrazine. A slight excess of peroxide is recommended to ensure complete destruction of the hydrazine. The addition of a trace amount of copper sulfate will catalyze the reaction, causing it to proceed more rapidly.

"For larger quantities, disposal is usually carried out by burning in increments in a small, concrete-lined pit. Hydrazine and aqueous solutions of hydrazine are placed in the pit by means of a pipe or surface channel. The hydrazine can be ignited by an igniter (squib-fired), an oxidizer such as nitrogen tetroxide, or a torch. Concentrations as low as 40 percent by weight hydrazine in water can be burned. Concentrations lower than 40% can be burned by enriching the dilute mixture with a soluble flammable liquid, such as alcohol."

Table IX. Decontaminants for Hydrazine Investigation

Decontaminant	Possible Reaction Products	Approx. Heat Liberated Kcal/Mole N_2H_4
H_2O	$N_2H_4 \cdot xH_2O$	3.9
$NaHCO_3$	$(N_2H_5)_2CO_3 \cdot Na_2CO_3$	10
H_3BO_3	A salt	5
$KMnO_4$	N_2	177
H_2O_2	NH_3, N_3H	91-121
Cl_2 gas HTH	N_2	160/177

* F. E. Scott, J. J. Burns, and B. Lewis, "Explosive Properties of Hydrazine." Report on Investigations 4460, U.S. Dept. of the Interior, Bureau of Mines, Pittsburgh, Pa., May 1949.

2. Monomethyl Hydrazine (Source of information: Olin Chemicals)

"To reduce fire hazards, spilled MMH may be diluted with large amounts of water and neutralized by dilute hydro-chloric acid

or sulfuric acid. This procedure ensures the trapping of MMH vapors and forms a MMH-type salt.

"Diluted MMH, while no longer a fire hazard, may still be dangerous if not disposed of properly. MMH must not be permitted to drain into a potable water system. Provisions must be made to permit liquid drainage into a disposal area where it may be burned in small increments or decomposed by a chemical decontaminant such as calcium hypochlorite (HTHtm) or hydrogen peroxide.

"Empty drums and containers should be rinsed with water and steamed for 15 minutes to remove toxic and flammable vapor."

3. UDMH (here referred to by the trade name "Dimazine") (Source of information: FMC Corp.)

"Equipment can generally be decontaminated rather simply by thorough flushing with large volumes of water or with dilute acid. It may be conveniently steamed thereafter. It should, of course, be thoroughly dried prior to return to Dimazine service, making sure that no water has been trapped at low points in the system.

"Our suggestion for deliberate destruction of comparatively large quantities of Dimazine is to burn it under proper supervision and safeguard. This technique has been successfully used in the field. Small quantities such as minor spills, etc., usually can be disposed of most conveniently through sewerage with water.

"Copious water flushing is recommended for personnel decontamination."

4. Hydrogen Peroxide (Source of information: Manufacturing Chemists Association)

"Hydrogen peroxide is an exceptionally pure product and contains no contaminants that would cause surface water pollution, or interference with sewage. Its decomposition products are pure water and oxygen. However, strong hydrogen peroxide should be diluted with copious

quantities of water before disposal to prevent strong reaction with organic materials and to prevent injury to fish life since there is some evidence that high concentrations of hydrogen peroxide are harmful to certain fish. (See "Treatment of Waste Waters Containing Hydrogen Peroxide, Hydrazine, and Methanol," Chemistry and Industry, 1951, 1104-6.) Since certain agencies of local, State, and Federal governments have been established to protect our streams, all rules and regulations applying to a given location should be ascertained and observed.

"The treatment of a decomposing container of hydrogen peroxide will depend upon several factors, such as the stage at which the decomposition is first discovered, the degree of contamination as indicated by the rate of temperature rise and the volume of hydrogen peroxide concerned. It should be noted that the rate of decomposition increases exponentially with temperature, 1.5 times for each 10° F. rise. Any container of hydrogen peroxide, if grossly contaminated, might rupture from decomposition pressure, or be subject to vapor explosion above the peroxide, if excessive temperatures are reached ...

"A drum of unstable hydrogen peroxide should be taken quickly to an isolated place, uncapped, and either overflowed with a water hose or tipped over and emptied as fast as possible, washing the peroxide away with plenty of water. However, if it has reached the point of boiling, or spewing steam from the vent, personnel should evacuate to a safe distance since the drum will probably rupture violently within a few minutes. When this occurs the area should be washed down liberally with water.

"A decomposing tank of hydrogen peroxide requires different treatment. Decomposition is evidenced by self-heating or bubble action. The addition of phosphoric acid (reagent grade - 1 lb. for each 100 gals. of H₂O₂ solution) may arrest the decomposition at this early stage. The tank should be watched closely and precautions taken in case decomposition is not checked.

"If the temperature of the tank continues to rise its contents should be disposed of before it reaches a point 15° F higher than the surroundings. A clean fire hose, without brass or iron fittings, should be inserted through the tank manhole to the bottom of the tank and the tank's contents diluted with a large amount of water and discharged as fast as possible by overflowing through the manhole or other means. This whole operation is facilitated if the tank is equipped with an aluminum deluge pipe reaching to the bottom of the tank with a remote coupling for water. In any event, loss of the peroxide is preferable to loss of the tank itself.

"Discarded peroxide from either a drum or tank should go to an open body of water or drainage ditch, preferably containing water. If any peroxide goes into a sewer or closed drain, there should be no combustibles and large volumes of water should be added to the drain along with the peroxide."

5. Nitrogen Tetroxide (Source: Hercules Inc.)

"Spills should be flushed to a collection sump and neutralized with soda ash or other alkali."

Also, "Transfer to salvage vessel. Neutralize with soda ash or lime. Keep from sewer or streams."

6. Nitric Acid

(First source: Manufacturing Chemists Association)

"Dilute and neutralize before disposal. Do not flush down drains where the acid will eventually pollute streams, city sewage systems, etc."

(Second source: Hercules Inc.)

"Neutralize with soda ash or lime."

IV. DISPOSAL RECOMMENDATIONS FROM THE TRW STUDY

All material in this section is taken directly from TRW Report No. 21485-6013-RU-00, prepared for the Environmental Protection Agency, by R. S. Ottinger et al (see the Literature Survey, Section II above.)

1. Hydrazine

Hydrazine as a waste will generally be encountered as excess material, as contaminated material from spills, or in aqueous streams from chemical process industries. Because of the hazards involved (unpredictable decomposition), hydrazine is usually not recovered in a concentrated form from contaminated or dilute systems. In ponds or holding tanks dilute hydrazine is decomposed by the air and bacteria into nitrogen, hydrogen, water and ammonia. In a concentrated form, hydrazine is destroyed by burning.

The safe disposal of hydrazine is defined in terms of the recommended provisional limits in the atmosphere, water and soil. These recommended provisional limits are as follows:

<u>Contaminant in Air</u>	<u>Provisional Limit</u>	<u>Basis for Recommendation</u>
Hydrazine	0.01 ppm	0.01 TLV
<u>Contaminant in Water and Soil</u>	<u>Provisional Limit</u>	<u>Basis for Recommendation</u>
Hydrazine	1.0 ppm	Quantity will rapidly oxidize to near-zero concentration

Hydrazine is generally destroyed by oxidation to water and nitrogen. In dilute solution, dissolved oxygen, catalysis, or bacterial action convert hydrazine to nitrogen, hydrogen, ammonia and water. Therefore, there are no problems in dealing with the products from waste treatment.

Current disposal practices for hydrazine are briefly described in the following paragraphs together with recommendations as to adequacy.

Option No. 1 - Open Pit Burning

Hydrazine poured into an open lined pit is burned to nitrogen and water. The transfer of the hydrazine and the ignition must be accomplished by a remote means. For drum quantities of hydrazine this method is generally acceptable although since excessive NO_x might be generated another option would be preferred.

Option No. 2 - Incineration

The Air Force has a minimum of ten trailer-mounted incinerators capable of incinerating up to 6 GPM of hydrazine in a variety of mixtures with water (from 100 percent hydrazine to 100 percent water). The effluents from the units is limited to 0.03 lbs/min NO_x when incinerating hydrazine. These units are acceptable for disposing of large quantities of hydrazine.

Option No. 3 - Catalytic Decomposition

One of the applications for hydrazine is its use as a monopropellant. When hydrazine is passed over a support (usually aluminum oxide) coated with certain metals or metal oxides, it is decomposed into nitrogen, hydrogen and ammonia. The details of catalyst composition are usually found in the classified literature. In most cases the catalyst is expensive, but TRW Systems has preliminary data on a low cost catalyst that should be further investigated.

Recommended Treatment: Controlled incineration with facilities for effluent scrubbing to abate any ammonia formed in the combustion process.

2. Hydrogen Peroxide

Concentrated hydrogen peroxide is a powerful oxidizing agent. Rapid decomposition is hazardous. Wasted concentrated hydrogen peroxide can be disposed of by dilution with water to release the oxygen. Agitation would accelerate the decomposition. After decomposition, the waste stream may be discharged safely.

3. Nitric Acid

Waste streams containing acids, acidic oxides, or bases can be treated by neutralization (1) to form a neutral solution which can then be discharged safely, or (2) to yield an insoluble precipitate which can be removed by filtration.

For the acids, acidic oxides and halides, soda ash-slaked lime solution is most commonly used. In the case of nitric and hydrochloric acids, the neutral solution of nitrate or chloride of sodium and calcium is formed and can be discharged after dilution with water.

Ammonium hydroxide may be neutralized by nitric acid to form a solution of ammonium nitrate which can be used as fertilizer.

Nitric acid forms a constant-boiling azeotrope with water (68% HNO_3 + 32% H_2O). The normal boiling point of the azeotrope is 120.5°C . Hence, under certain conditions, spent nitric acid can be recovered by steam distillation to yield concentrated acid.

Recommended treatment: Soda ash-slaked lime is added to form the neutral solution of nitrate of sodium and calcium. This solution can be discharged after dilution with water.

V. CURRENT DISPOSAL PRACTICES

This section lists, propellant by propellant and company by company for each propellant, the actual current disposal practices for each "user" organization, insofar as we have been able to ascertain them. In order to facilitate our access to frank, correct, and detailed information, all of these organizations were promised that the information furnished would not be identified as to source. For that reason, all organizations are referred to below in terms of a number rather than by the organization name. A total of eighteen organizations are represented in this section; the other organizations listed earlier under "Positive Replies" include chemical manufacturers, other organizations that provided us with general advice on disposal methods rather than being able to describe current activities of their own, and disposal activities described separately in Sub-section G below, "Disposal at the Eastern and Western Test Ranges." It is our belief that these eighteen organizations account for virtually all of the propellant disposal activity currently being carried out in this country outside of ETR and WTR. It should be emphasized that the code numbers are used in this report only in the case of organizations actually describing their own current disposal activities.

The overall level of activity in hypergolic propellant disposal is clearly much lower now than several years ago; some organizations that formerly handled large quantities of these propellants as part of their everyday routine have not handled significant quantities for some time, and many of the people who were most familiar with propellant disposal practices have moved on to other positions of out of the aerospace industry. On the other hand, those organizations still involved with hypergolic propellants have by and large improved and refined their disposal practices considerably over the past several years.

In the list that follows, the treatment of hydrazines posed a problem. We are specifically interested in four types of hydrazine propellants: N_2H_4 , MMH, UDMH, and Aerozine 50 (50% N_2H_4 , 50% UDMH.) Most disposal practices, however, do not differentiate between the various hydrazines - an incinerator or holding pond used for hydrazines, for example, will normally be used for any

of the hydrazines needing disposal, without discrimination. For that reason, the following list first treats disposal methods that seem to be used for any hydrazine the organization needs to dispose of. The following sections pertaining to specific hydrazines include only additional information not included in the first section. There is no separate section for Aerozine 50 or UDMH, since we have discovered no disposal techniques that are specifically applicable to these propellants and not to other hydrazines.

Primary attention on the part of most of the cooperating organizations was given to liquid disposal, as indicated below, with vapors often simply vented to atmosphere. N_2O_4 is the only propellant of interest that will boil away if left unpressurized in a warm environment (its boiling point is $70.1^{\circ}F$ ($21.15^{\circ}C$) at 1 atm), although RFNA gives off NO_2 vapors (the "fumes"). UDMH has the lowest boiling point of the three hydrazines: $146^{\circ}F$ ($63^{\circ}C$) at 1 atm.

Past practices (since discontinued) mentioned by several organizations, such as pouring waste propellants on the ground in remote areas, etc., are not included in the following list. In addition, simple venting of vapors to the atmosphere and transferring deluge water to holding ponds were mentioned by several organizations in connection with all the propellants, and are also not included in the list. The more significant current practices that were reported to us are listed below. In most cases, the descriptions are based directly on written or verbal descriptions given to us by representatives of the organizations concerned. In a few cases, they are based on our own facility visits and first hand observations.

A. HYDRAZINES - GENERAL

1. Liquid

- #1 burns small quantities in air or with N_2O_4
- #2 dilutes concentrated wastes with water (at least to 50%) and burns with excess air in a combustion chamber designed for the purpose. The combustion is initiated by a fire-brick heat sink which is preheated with propane to provide positive ignition and insure complete combustion. Water based flush fluids and similar low concentration wastes are dumped into one of two holding ponds. One is a square pit agitated by bubbling compressed air at two

points; the other is a ditch extending about one mile past the point at which it last receives effluent. Because of addition of oxidizer wastes to the same holding ponds, the contents are normally acidic; automatic monitoring and neutralizing stations at each pond measure the pH and add NaOH solution until the pH exceeds 6.5. At this point, the station automatically begins pumping fluid from the pond over the dam until the pH again drops.

- #3 burns waste hydrazines in an incinerator, by over-stoichiometric burning followed by a water quench to 2000^oF and reburning to eliminate CO and H₂ products.
- #4 dilutes amounts of less than one gallon with water and neutralizes. Quantities larger than one gallon are disposed of through "licensed disposal companies." Some wastes are consumed by burning if the propellant plus contaminant will support combustion.
- #5 uses large enough quantities that it is feasible to mix out of specification hydrazines back in with the main supply without seriously degrading the main supply. They have also disposed through combustion in a simulated rocket engine with N₂O₄.
- #6 uses open pit burning in a remote area; combustion is initiated by throwing in a burning towel. In addition, spills are flushed with volumes of water to a concrete-lined lagoon, where hydrogen peroxide and copper sulfate catalyst are added.
- #7 uses a water deluge system and a large fume scrubber to capture all hypergols. They are neutralized in underground sumps and then consigned to a disposal contractor equipped with tank trucks for final disposition. They can also be used to neutralize the nitric acid effluent from N₂O₄ vapor scrubbers- see the description under N₂O₄ vapors.

- #8 disposes of small quantities by burning; larger quantities are turned over to another organization on this list for disposal in an incinerator.
- #9 disposes of aqueous solutions with hydrazine concentrations between 1% and 40% in an incinerator, fired by diesel fuel, at 2700^o F. Contaminated fuels, (which may contain small amounts of oxidizer or flush fluids) are collected in a holding pond, diluted to 40% fuel or less if necessary, and fed to the incinerator. Wastes with less than a 1% concentration of fuel are chemically treated as follows:
- (1) .01 pound of copper sulfate is added for each 1000 gallons of waste.
 - (2) The pH is adjusted to between 7.0 and 8.5 by adding a 50% solution of NaOH, or nitric or sulfuric acid, as required.
 - (3) Hydrogen peroxide (35% strength) is added.
 - (4) After mixing, the fuel concentration should be less than 0.5 ppm, and the pH between 6.0 and 8.0. If so, the wastes are surface drained; if not, the procedure is repeated starting at step (2).
- #10 flushes with water and drains to an open sump; contaminated propellant may also be added directly to the sump. Contents of the sump are periodically disposed of in an incinerator, fired by natural gas, at 1900^o F.
- #11 uses four 300,000 gallon oxidation ponds. Oxidation is by air contact at the pond surface (not aeration, although this modification is being considered). Oxidizer wastes, when available, are transferred to the same ponds. The ponds are sometimes emptied when the concentration of MMH is at or below 1 ppm, although evaporation at this site is far more important than rainfall and the ponds are usually allowed to sit even after the hydrazine content is no longer measurable.

#12

on the other hand, is in an area where heavy rainfall predominates, and mechanisms were required to quickly decompose the hydrazine in their 500,000 gallon holding pond to allow liquid removal prior to overflow. The solution was an aeration system consisting of two large H-shaped manifolds in the bottom of the pond. The manifolds are supplied with either air from a compressor, or bottled oxygen. Very large bubbles are generated, and considerable liquid motion throughout the pond results. In addition, catalysts (both copper sulfate and rusty steel containers) have been used, and chlorine gas can be bubbled into the pond. The pond is concrete, 8-10 feet deep with sloping sides, and the normal mode of operation is with compressed air. Oxidizer wastes can be added to the same pond, but are not normally encountered.

2. Vapors

#2

vents to atmosphere but does not risk releasing unless atmospheric conditions will reduce contaminant concentrations below threshold limit values. This determination is based on data taken at micrometeorological stations at each vent site, on wind direction, velocity, gustiness, and thermal lapse rate at 2 ft., 50 ft. and 100 ft. from ground level. Prediction is based on standard mixing models, modified by empirical corrections for local conditions.

#5

pressurizes vapors with N_2 and vents through a scrubber. Water from the scrubber is flushed down trenches to a 100,000 gallon concrete holding pond, which is agitated by a recirculating pump. pH in the holding pond is normally on the acid side; NaOH is added to neutralize it and a reagent used to check for free hydrazine radicals. If too high a concentration is present, copper sulfate and dilute H_2O_2 are added. When the contents look good, they are pumped out to a series of holding ponds stairstepping down the side of a hill, all of

which are continually monitored. Deep water wells in the area are also periodically checked. (This system relies on abundant supplies of water and good laboratory backup). The scrubber is a 14 inch diameter stainless steel pipe, 20 feet long, with water spray. Originally, a stainless steel tub with a tall stack was tried, as well as a recirculating NaOH spray rather than water spray. Another variation is an aspirator, in which vent vapors are entrained in the water flow at a number of low pressure points.

#6 vents to atmosphere using a large blower. A small weather station at the test cell monitors wind velocity and direction, and venting is carried out only if the wind is in a favorable direction and above a specified minimum velocity.

#7 uses fume scrubbers - see above under Liquids.

B. ANHYDROUS HYDRAZINE (N_2H_4)

1. Liquid

#13 dilutes 100 to 1 with water and drains into the ground. A neutralization system consisting of a series of trenches and two 1500 gallon holding tanks is being constructed. The material in the holding tanks will be neutralized with a 12 1/2% solution of sodium hypochlorite. When free Cl is sensed in the solution the neutralized material will be drained from the tanks to a pond.

#14 burns off small quantities in a 10 ft. by 20 ft. steel pan, ignited by a gas flame.

C. MONOMETHYL HYDRAZINE (MMH)

1. Liquid

#7 neutralizes small amounts using hydroxyacetic acid.

#8 flushes residuals with isopropyl alcohol and transfers to another organization on this list for disposal in an incinerator.

D. HYDROGEN PEROXIDE (H_2O_2)

1. Liquid

- #1 pours on bare ground and flushes with water
- #5, #6, #9, and #11 use H_2O_2 to aid in disposal of hydrazines, and for treating holding ponds.
- #15 disposes of small quantities in the laboratory using a platinum or silver screen as catalyst. Large quantities are diluted with water to between 25% and 40% H_2O_2 and decomposed by catalyzing with caustic. At 212°F and a caustic level of 0.5 - 1% NaOH, decomposition is more than 95% complete in one hour.
- #16 has diluted small quantities with water and discarded to the drainage system.

E. NITROGEN TETROXIDE (N_2O_4)

1. Liquid

- #1 dilutes with water and neutralizes with sodium carbonate, or alternatively burns with hydrocarbons or other fuels.
- #2 pre-dilutes with water and dumps into the same holding ponds that receive dilute hydrazines; see Hydrazines - General for additional description and treatment.
- #4 treats as described under Hydrazines - General
- #5 dilutes and adds to holding pond - see Hydrazines - General for additional description and treatment. Alternatively, allows to vaporize; see following section for treatment of vapors.
- #6 pours small quantities into the concrete-lined lagoon mentioned above under Hydrazines - General. Alternatively, it is allowed to vaporize and treated as described in the following section.

- #7 has neutralized small quantities with triethanolamine. Larger quantities (roughly 8 gallons) caused violent reaction with triethanolamine, and explosion. Currently both neat N_2O_4 and halocarbon solvent contaminated with N_2O_4 are shipped to the NASA facility at White Sands, N. M. for disposal. This organization also attempted to use Molecular Sieve 13X material, on the recommendation of another organization; their experience was that the material is permanently degraded by N_2O_4 contact and that violent reaction is likely.
- #8 transfers their waste to other organizations on this list for disposal. In addition, small quantities are wiped up with a neutralized (sodium bicarbonate) wet sponge. The sponges are then placed in a neutralized solution contained in a stainless steel bucket. This solution is subsequently disposed of by a commercial disposal service. Residuals are flushed with Freon MF and dumped into a holding tank for later disposal by a commercial disposal service company.
- #9 dilutes to less than 5% concentration and neutralizes with caustic. The waste is then pumped into the ocean.
- #11 adds oxidizer wastes to the same holding ponds described above under Hydrazines - General.
- #17 has returned N_2O_4 to Hercules Inc.

2. Vapors

- #2 vents to atmosphere, with the same precautions as described under Hydrazines - General.
- #5 pressurizes vapors with nitrogen gas and sends them through a scrubber as described under Hydrazines - General (not the same unit, of course) and thence to the system of holding ponds previously described.

- #6 vents vapors through a propane-fueled flare.
- #7 captures small quantities of N_2O_4 vapors by sparging through water drums. The contaminated water is then shipped to the NASA facility at White Sands, N. M., for disposal. This organization also uses a large water scrubber of their own design. Water enters through a series of downward-pointing spray nozzles, with layers of stainless steel shavings below each nozzle to slow and hold the water. The effluent, which is dilute nitric acid, is neutralized after it leaves the scrubber, either chemically or by mixing with diluted hydrazine fuels.
- #11 and #12 have both used propane-fueled flare burners in the past, but no longer use these units.

F. INHIBITED RED FUMING NITRIC ACID (IRFNA)

1. Liquid

- #1 dilutes with water and then neutralizes with sodium carbonate.
- #2 treats in the same way as N_2O_4 .
- #4 same treatment as hydrazines and N_2O_4 , except that water scrubbing of the combustion gases is needed for removal of HF emissions.
- #16 has in the past absorbed and neutralized small quantities in an alkaline solution, with the spent solution being discarded to the drainage system.
- #18 neutralizes spills from leaking rocket motors using a suitable alkaline.

G. DISPOSAL AT THE EASTERN AND WESTERN TEST RANGES

Current (and recent) propellant disposal operations at the Eastern Test Range are primarily associated with one of three programs: Saturn, Titan, and Delta. In all three cases, vapor disposal occurs at the launch site, with liquid wastes being transferred to the service contractor, Pan American World Airways, for disposal elsewhere. Pan Am's disposal operations are included in the coded list above.

The three vapor disposal operations are all different. Both Saturn and Titan launch operations vent to atmosphere, Saturn through large trailer-mounted blowers and Titan through a tall stack (N_2O_4 only - hydrazines are vented directly to atmosphere), while scrubbers are used at the Delta launch pad.

The blowers used for Saturn operations are large trailer mounted units with air flow capacities of 190,000 cfm each. Vent vapors - Aerozine 50 and N_2O_4 vapors are fed to trailers situated on opposite sides of the pad - pass through liquid-vapor separators and then are introduced into the air streams produced by three large fans on each trailer. The primary purpose of the fans is dilution, although the plume on the oxidizer side is still said to be highly visible, indicating a concentration of over 75 ppm in the plume. Maximum vapor flow rates are 0.2 pounds per minute fuel, 1.9 pounds per minute oxidizer.

The oxidizer vent stack at the Titan facility is a four inch diameter stainless steel tube, approximately 200 feet high. This facility also uses a 28,000 gallon tank for oxidizer wastes, and a small concrete holding pond for fuel wastes, both of which are emptied periodically by the service contractor. The preferred approach for oxidizer spills is to allow them to evaporate, rather than flushing with water to create a nitric acid waste.

The Delta facility uses a water scrubber for hydrazine vapors, and a baking soda (5% NaHCO_3 solution) for nitrogen tetroxide vapors. Both scrubbers are physically small (four to six feet high) and the liquid effluents from both are allowed to run into a concrete holding pond.

At the Western Test Range, the major difference is that there is no service contractor to whom waste propellants can be transferred for disposal. Propellant use is primarily associated with Titan and Delta operations.

At the Delta launch site, identical scrubbers to those used at the Eastern Test Range have been installed, but are not in use. A small concrete holding pond has recently been installed just downhill from the pad for spills, contaminated wastes, etc. Venting is to the atmosphere.

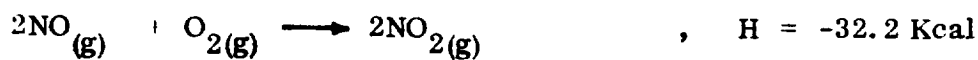
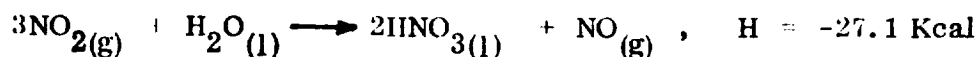
At the Titan facility, N_2O_4 vapors are vented through a propane-fueled flare burner, and the hydrazine vapors are vented directly to atmosphere if wind direction and velocity are satisfactory. Adverse wind direction or lack of wind can shut down operations. A 3 knot minimum wind velocity is observed for operation of the flare burner to preclude local accumulation of toxic vapor in case of flame-out. Liquid hydrazines are disposed of by diluting between 3 and 5 to 1, transferring to a water pit, and neutralizing with a 16% sodium hypochlorite solution. Each pad has a holding tank, and it is possible to burn up to two gallons at a time in small basins, although this has not been done in many years. Quantities of greater than thirty gallons are supposed to be taken by tankers to the U.S.A.F. for disposal, but this course of action has not been necessary.

The Air Force does not have any means of disposing of waste propellants at Vandenberg, but is experimenting with spray aeration at a small concrete holding pond.

H. COMMERCIAL MANUFACTURE OF NITRIC ACID

One method for removing N_2O_4 vapors from pressurization gas is absorption (scrubbing). This process is similar to the one used commercially to manufacture nitric acid from NO_2 . It may be economically feasible to produce usable nitric acid from the waste by using gas absorption.

Commercial nitric acid is manufactured by introducing NO_2 gas into an absorption tower. The two dominating reactions are:



There is an air rich environment in the tower to promote the oxidation of NO .¹

The oxidation of the nitric oxide to nitrogen dioxide is the slowest reaction with its equilibrium most favorable at lower temperatures. The reaction is usually carried out in absorbers with considerable capacity and provided with cooling. Because of the decrease in volume this reaction is favorable under pressure according to Le Chatelier's principle.

The reaction: $3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO}$ is a gas absorption phenomenon. This reaction rate is the limiting factor for sizing the scrubber. The reaction rate is increased by employing an absorption tower under pressure, cooling the tower and using counter current air flow.² The rate can also be increased by using packing such as Raschig rings or Berl saddles. Packing is used to increase the surface area or expose new liquid to the surface, thus increasing the rate of absorption. If the absorption tower is operated at atmospheric pressure an acid containing 50-55% HNO_3 can be produced.

¹Clark, R. L., W. L. Faith and D. B. Keys, Industrial Chemicals. John Wiley & Sons, Inc., New York, 1950.

²Shreve, R. N., Chemical Process Industries. McGraw-Hill, New York, 1956.

VI. SPECIALIZED EQUIPMENT AND OTHER SOLUTIONS

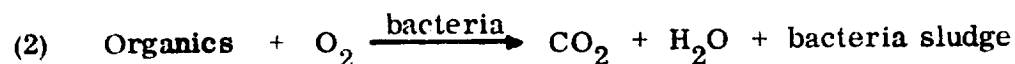
Of the many incinerators now on the market, at least a few seem suitable for propellant disposal. Two have seen considerable use for this purpose already. One, designed by Thermal Research and Engineering Corp., of Conshohocken, Pa., has been in use at Cape Canaveral over a decade and still seems to be giving very satisfactory performance; it has been used for aqueous solutions of hydrazines and N_2O_4 , and for hydrocarbon fuels. Thermal has not designed any other incinerators for this purpose since then, but is still active in burner design and emissions control. Another incinerator, built by Hirt Combustion Engineers of Montebello, California, in 1968 for one of the companies we contacted, is still in active use for disposing of aqueous solutions containing hydrazines and has also been used for hydrocarbon fuels and exhaust gas. In addition to these, the Marquardt Company of Van Nuys, California markets commercial fume incinerators and liquid incinerators which are an outgrowth of their work in aerospace propulsion, and have run tests on disposal of N_2H_4 , UDMH, and N_2O_4 in their Sudden Expansion (SUE) incinerator. More detailed descriptions and evaluations of all these incinerators are presented in the section of this report covering Phase 2, Evaluation of Current Disposal Methods.

A related development, by Martin-Marietta Corp., Denver, Colorado, is a propane-fueled, orificed circular burner. This flare burner has only been used for N_2O_4 vapors, although it could perhaps be modified to handle hydrazine vapors. It is also covered at length in the section on Phase 2. TRW Systems, Redondo Beach, California, suggested "consideration of the concept of burning the propellants in a work horse engine. Such a capability is available at TRW although it has not been used specifically for disposal of propellants."

TRW also commented that filtration through a simple filter screen or strainer is often successful in removing suspended particulate matter and returning propellants to specification.

Shell Development Company's Chemical Research Laboratory in Houston, Texas, commented, "Although one of our customers in West Germany has indicated that they successfully used Shell 405 Catalyst to remove traces of hydrazine from organic process streams, we do not consider its use for disposal purposes as economical (the catalyst currently sells for \$2950.00 per pound and is subject to poisoning by chemical impurities)."

The use of H_2O_2 in sewage treatment was described by Du Pont in the article mentioned in the Literature Survey, Section II. The H_2O_2 provides an additional form of oxygenation or aeration to satisfy metabolic requirements of micro-organisms. The reactions are:

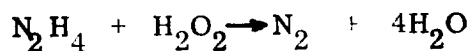


The H_2O would be especially effective during periods of mechanical failures or overloads.

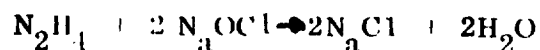
Allied Chemical Corp., Solvay, New York, recommended the following procedure for the disposal of IRFNA: "Unwanted material may be disposed of by addition to a large volume of water containing an alkali such as caustic soda or soda ash to neutralize the acid and calcium chloride to precipitate the fluoride. The mixture should be settled and checked to be sure the pH is 7 or higher before decanting to waste. The sludge should be taken to a landfill area for disposal."

Fisons Ltd. of Harston, Cambridge, England, a hydrazine manufacturer, recommended the following reactions for disposal of concentrated hydrazine solutions:

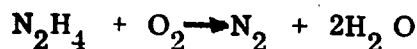
(1) With alkaline H_2O_2 in the presence of iron or copper (II) salts.



(2) With excess sodium hypochlorite:



(3) With atmospheric oxygen in the presence of copper (II) salts.



A few manufacturers stated that there might be limited possibilities for recycling contaminated propellants. Hercules Inc. wrote, "We could possibly rework N_2O_4 to reduce water content and adjust oxides content. Some contaminants, however, may not be acceptable in our plant. Each rework would probably require prior submission of an analysis showing impurities and a sample for our verification." They further stated that IRFNA reprocessing would be impossible because of the hydrofluoric acid.

Similarly, PPG Industries expressed possible interest in reworking hydrogen peroxide, and Fairmount Chemical Co., Inc. is interested in purchasing N_2H_4 "unmixed with other compounds."

EVALUATION OF CURRENT DISPOSAL METHODS (PHASE 2)

	Page
I. INTRODUCTION.....	62
II. DISPOSAL OF LIQUID HYDRAZINES.....	63
A. INCINERATION.....	63
B. OPEN PIT INCINERATION.....	87
C. CHEMICAL TREATMENTS.....	88
D. DILUTION/AIR OXIDATION/BACTERIAL ACTION.....	96
E. OPEN BURNING.....	100
F. OCEAN DUMPING	101
G. POURING DIRECTLY ON OPEN GROUND.....	101
III. DISPOSAL OF HYDRAZINE VAPORS.....	103
A. INCINERATION	103
B. VAPOR SCRUBBING.....	107
C. VENT TO ATMOSPHERE.....	108
IV. DISPOSAL OF LIQUID NITROGEN TETROXIDE (DINITROGEN TETROXIDE - N_2O_4).....	110
A. INCINERATION.....	110
B. CHEMICAL NEUTRALIZATION.....	124
C. SIMPLE DILUTION WITH WATER.....	129
D. DISPOSAL AS A VAPOR.....	131

	Page
V. DISPOSAL OF NITROGEN TETROXIDE VAPORS	132
A. FLARE BURNERS	132
B. SCRUBBING - ABSORPTION IN WATER	136
C. SCRUBBING - ABSORPTION IN NaHCO_3	137
D. ATMOSPHERIC VENTING.....	138
VI. DISPOSAL OF LIQUID IRFNA.....	141
A. GENERAL REMARKS	141
B. INCINERATION.....	141
C. CHEMICAL TREATMENT.....	142
D. H_2O DILUTION	145
VII. DISPOSAL OF IRFNA VAPORS.....	147
A. INCINERATION	147
B. SCRUBBING	148
C. ATMOSPHERIC VENTING	149
VIII. DISPOSAL OF LIQUID HYDROGEN PEROXIDE	151
A. CHEMICAL DECOMPOSITION.....	151
B. BIOLOGICAL DISPOSAL.....	158
C. POURING ON THE GROUND	159
IX. DISPOSAL OF H_2O_2 VAPORS	160
A. ATMOSPHERIC VENTING.....	160

1. INTRODUCTION

Phase 2 was concerned with evaluation of current disposal methods, primarily in terms of their effects on the environment. The objective was to identify those methods suitable for further application as new disposal needs arise, and to identify requirements for new technology, if they exist, or areas where advances in the state-of-the-art offer especial promise. This study was not concerned with identifying any specific current environmental problems.

The sections that follow describe and discuss all of the current disposal methods identified during Phase 1, starting with those used for the hydrazine fuels and proceeding to nitrogen tetroxide, inhibited red fuming nitric acid, and hydrogen peroxide, in that order. In order to avoid repetition, material that is pertinent to more than one disposal method, or more than one propellant, is usually presented just once when it first comes up, with the result that the earlier sections are as a rule more comprehensive than the later ones.

In the case of IRFNA disposal, we departed somewhat from our rule of treating only disposal methods actually in current use, as IRFNA usage in significant quantities is practically nonexistent at the present time, as far as we could determine. However, the combination of the close similarities between IRFNA and N_2O_4 , and between IRFNA and concentrated nitric acid, led us to the conclusion that potential disposal methods for IRFNA can, in many cases, be evaluated on the basis of current experience. (Oxides of nitrogen and their chemical and photochemical reactions in the atmosphere have been studied intensively in recent years, and nitric acid is used in large quantities by the chemical industry.) The special problems associated with the HF content of IRFNA are treated in the portion of this report on Application Studies (Phase 3).

The reader's attention is also called to the condensed evaluations that were presented in Tables I through IV of the Summary Report section, pages 12 through 17 of this report.

II. DISPOSAL OF LIQUID HYDRAZINES

A. INCINERATION

II. A. 1. Current Applications

In Phase 1 of this study, it was found that two organizations are currently incinerating aqueous solutions of hydrazines and, in one particular instance, a solution of MMH in isopropyl alcohol. One incinerator uses natural gas as primary fuel and maintains a flame temperature of 1900 °F; the other uses diesel fuel and maintains 2700 °F or higher (3200 °F was also mentioned).

The TRW study¹ recommended controlled incineration with effluent scrubbing to eliminate any ammonia formed in the combustion process.

In addition to the two organizations actually using incinerators for the routine disposal of hydrazines, the Marquardt Company of Van Nuys, California, has done extensive development, testing and evaluation work on an incinerator for hydrazine fuels. The evaluation phase of the work was funded by the Air Force Rocket Propulsion Laboratory², and is described in greater detail under "bases for evaluation" below.

¹R. S. Ottinger, J. L. Blumenthal, D. F. Dal Porto, G. I. Gruber, M. J. Santy, and C. C. Shih, "Recommended Methods of Reduction, Neutralization, Recovery or Disposal of Hazardous Waste", Report No. 21485-6013-RU-00, TRW Systems Group, 1 February 1973, prepared for Environmental Protection Agency, Contract No. 38-03-0089. (See especially Vols. I, XII)

²Joel E. Hutson, "Toxic Waste Burner Evaluation", Final Report, AFRPL Contract No. F04611-73-C-0007 (Marquardt Company Report S-1271), November 1973.

11.A.2. Thermochemical Aspects

Incineration is a controlled combustion process to convert waste propellant to a less toxic, less bulky, less noxious or more easily disposable material. The principal undesirable incineration products from an environmental viewpoint are NO_x and CO . Occasionally, NH_3 or hydrocarbons or soot are released when operating under non-optimum conditions. Direct flame or catalytic destruction of waste propellants produce an effluent of N_2 , CO_2 and H_2O vapor which can be vented safely to the atmosphere. Undesirable compounds (such as NO_x) formed during incineration may require a secondary treatment, such as scrubbing, to lower their concentration to acceptable levels prior to atmospheric release.

Important criteria for an adequate disposal system of a waste propellant include the following:

- 1) The effluent should be inconspicuous and safe.
- 2) The system should not be prohibitively expensive to operate and maintain.
- 3) It must meet pollution standards.

Gas sampling techniques and analysis must be adequate to provide meaningful data. Factors to be considered are:

- 1) The sample must be representative.
- 2) The integrity of the sample must be preserved.
- 3) Initial cost and operating cost of equipment.
- 4) The possibility of biased interpretation and/or omission of test results in reports.

The variables which have the greatest effect on the completion of the oxidation of the propellant waste are:

- 1) Combustibility
- 2) Reaction Temperature
- 3) Residence Time in Incinerator
- 4) Gas Turbulence in Reaction Zone.

Hydrazine, UDMH, and MMH have low flammability limits. With

proper feed rates and the use of auxiliary fuels combustibility is readily controllable. Temperature can be controlled over some range by varying the air fuel ratio, and a well-designed incinerator will allow considerable excess air or secondary air to keep temperatures down.

Rates of oxidation reactions are increased rapidly by higher temperatures. A design range of 2400 °F to 3000 °F or higher may be specified depending upon the waste propellant being disposed. Three basic methods of controlling the combustion temperature are:

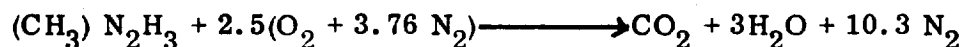
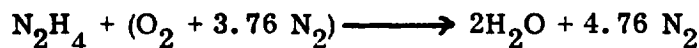
- 1) Excess Air Control
- 2) Two Stage Combustion
- 3) H₂O Injection.

Sufficient time must be provided during the waste incineration to allow droplets or particles to react with O₂ or oxidizers. From 0.1 to 1 second or more may be required. The evaluation of this time factor can only be made by tests of individual incinerators or from manufacturers' recommendations.

The degree of turbulence in the reaction zone significantly affects the incinerator performance. Intimate mixing of the air and waste propellant gases is required for completeness of combustion.

NO is a pollutant common to incineration processes which utilize air. NO formation results from O₂ and N₂ reacting at elevated temperature. Figure 1 presents graphically the thermodynamic equilibrium concentration of NO as a function of % excess air at various reaction temperatures for combustion of materials that do not contain nitrogen themselves. The incineration of hydrazine fuels would be expected to yield higher values than shown because they are high-percentage nitrogen containing compounds.

The stoichiometric combustion equations for hydrazine, MMH, and UDMH in air are, respectively ,



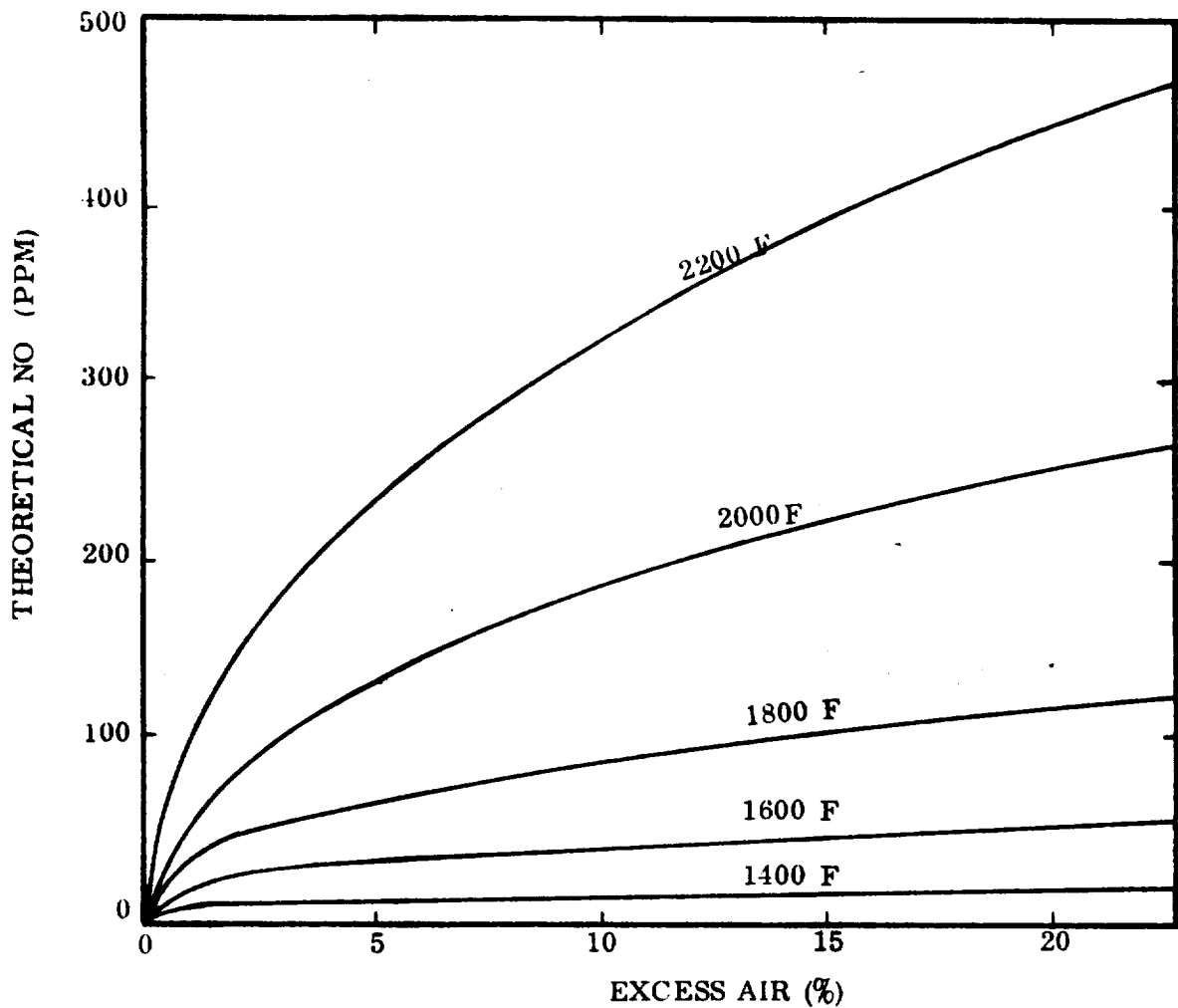
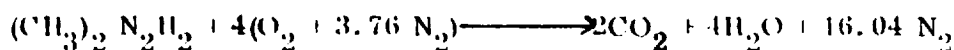
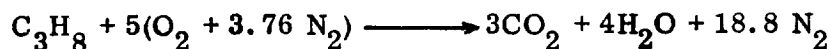


FIGURE 1
EQUILIBRIUM NO CONCENTRATIONS IN COMBUSTION EFFLUENTS

(R. D. Ross, Industrial Waste Disposal, Van Nostrand - Reinhold Corp., N. Y., 1968, p. 340; quoted by R. S. Ottinger et al, TRW Report No. 21485-6013-RU-00, 1973.)



In addition, the stoichiometric combustion equations for the auxiliary fuels methane (natural gas), propane, and butane are, respectively,



In a typical incineration process, one of the hydrazine fuels (or a mixture of two of them, such as Aerozine 50) is burned in air, in conjunction with natural gas (which is primarily methane) or liquified petroleum gas (propane or butane) as an auxiliary fuel used for preheating, start-up, and usually to maintain combustion in case of a somewhat irregular supply of the waste fuel. It should be noted that the auxiliary fuel has the effect of decreasing combustion temperatures, and acts as a reducing agent in the case of over-stoichiometric (fuel-rich) combustion and hence can prevent or alleviate the formation of oxides of nitrogen.

A starting point for the chemical description of the incineration of hydrazine fuels would therefore consist in simply adding the appropriate stoichiometric equations above. In actual practice, however, the complete description of the reactions is considerably complicated by the following factors:

- a) Non-stoichiometric mixtures and incomplete combustion result in the formation of partial products, such as carbon monoxide and ammonia, as well as allowing emission of unburned fuel.
- b) High combustion temperatures result in the dissociation of water and CO_2 , and in the formation of oxides of nitrogen.
- c) In some incinerators, the hydrazine fuels must be supplied as aqueous solutions, hence introducing additional H_2O in both sides of the equations and altering the equilibrium composition of the products.



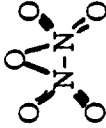
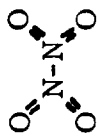
Hence a complete combustion description must include the possibility of formation of a number of trace products, including H_2 , O_2 , H , O , OH , CO , NO , NO_2 , N_2O , hydrocarbons (HC), NH_3 , amines (RNH_2) and unburned fuel: N_2H_4 , MMH, UDMH.

Of these trace products, the most serious are probably the fuels themselves. Emission of unburned fuels can be minimized by combustion chamber design (good mixing, high turbulence, long dwell times), by lean mixtures or secondary air injection, and by high combustion temperatures. Unfortunately, high combustion temperatures result in increased CO_2 dissociation (forming CO) and, perhaps more seriously, the formation of oxides of nitrogen as shown in Figure 1. Carbon monoxide formation can be reduced by use of excess air (lean mixtures) but this results in still greater formation of oxides of nitrogen. Long combustion chamber dwell times also aggravate the oxides of nitrogen problem.

The incinerator emissions problem is therefore quite similar to the automotive emissions problem: most of the steps that result in "cleaner", more complete combustion create additional problems in terms of the formation of oxides of nitrogen. Of these, N_2O is relatively harmless and NO_2 and N_2O_4 are not stable at elevated temperatures; NO , however, is poisonous, and will oxidize in the atmosphere to form NO_2 , the poisonous reddish-brown gas that is such a major air pollution factor. Table X presents additional information on the various oxides of nitrogen.

The problem is not an impossible one, however, and considerable progress has been made in vastly reducing both automotive and gas turbine emissions through improved combustion chamber design. Thorough mixing and turbulence seem to be beneficial from all points of view. Temperature problems can be alleviated by ensuring uniformity of temperature: that is, by eliminating hot spots which serve no functional purpose, but which can be responsible for a large fraction of the NO formation. Some control of residence time seems possible in gas turbine combustors (and, presumably, incinerators): NO formation is a function of time as well as temperature; if the time that a typical gas particle spends at elevated temperature can be controlled to the minimum value consistent with complete combustion, then NO emissions can

TABLE X
OXIDES OF NITROGEN

#	Name	Formula	N ₂ Valence	Structure	Solubility in H ₂ O		Remarks
					Cold	Hot	
1.	Nitric Oxide	NO	2	N=O	7.3cc 100 ml H ₂ O@0° C	2.4cc 100 ml H ₂ O@60° C	Common air pollutant
2.	Nitrous Oxide	N ₂ O	3		130cc 100 ml H ₂ O@0° C	51 cc 100 ml H ₂ O@25° C	Relatively inactive in air or with O ₃ . Not a pollutant.
3.	Dinitrogen Trioxide (Nitrous Anhydride)	N ₂ O ₃	4		Soluble	Dissociates	Unstable
4.	Dinitrogen Pentoxide (Nitric Anhydride)	N ₂ O ₅	6		Soluble	Dissociates to HNO ₃	Unstable
5.	Nitrogen Dioxide	NO ₂	4	O=N=O	Soluble in Alk.		Common air pollutant
6.	Dinitrogen Tetroxide (Nitrogen Tetroxide)	N ₂ O ₄	5		Soluble	Soluble	A dimer of NO ₂ . An equilibrium mixture of N ₂ O ₄ and NO ₂ (84/16 at 20° C)

be minimized. Thorough mixing has the added advantage of shortening the dwell time needed to insure complete combustion, by increasing the probability of early contact between an air molecule and a fuel molecule. In an incinerator there is no need for a high exit temperature, so that a water quench is a possible means of controlling dwell time. Alternatively, secondary air (air added downstream of the primary combustion zone) might be used to bring the temperature to a level too low for NO formation, but high enough for some of the combustion reactions to go to completion.

II. A. 3. Environmental Standards

Existing standards and limitations are based primarily on toxicity data, which can be presented in various forms depending on length of exposure, etc. For the safe disposal of waste propellants, the acceptable criteria for release into the environment are defined by the limits in Table XI. Most of these data were obtained from publications of the American Conference of Governmental Industrial Hygienists (ACGIH) and Occupational Safety and Health Administration (OSHA) tables. Other sources include the National Academy of Science/National Research Council's Committee on Toxicology (NAS/NRC), and the American Industrial Hygiene Association (AIHA). Much of the original data has been collected in the "Hazards of Chemical Rockets and Propellants Handbook"³ prepared under the auspices of the Joint Army, Navy, NASA, Air Force (JANNAF) Propulsion Committee.

The Threshold Limit Values (TLV) refer to the concentrations of an airborne constituent to which nearly all workers may be exposed repeatedly, day after day without adverse effect. The TLV represents a time-weighted concentration for a 7 or 8-hour workday and 40 hour work week.

Emergency Exposure Limits (EEL) are limits applied to protect industrial workers should an emergency (accident) situation occur.

"Skin warning" refers to the potential contribution to the overall

³ Volume III, "Liquid Propellant Handling, Storage and Transportation", AD 870259, CPIA/194, May 1972.

TABLE XI
TOXICITY LEVELS

EEL														
Constituent	TLV		5 minute exposure		10 minute exposure		15 minute exposure		30 minute exposure		60 minute exposure		Source	Skin Warning
	PPM	mg/m ³	ppm mg/m ³		ppm mg/m ³		ppm mg/m ³		ppm mg/m ³		ppm mg/m ³			
			---	-----	---	-----	---	-----	---	-----	---	-----		
N ₂ H ₄	1	1.3	---	-----	30	39	---	-----	---	-----	10	13	NAS/ NRC	Yes
MMH	0.2	0.35	---	-----	90	158	---	-----	---	-----	15	26	NAS/ NRC	Yes
UDMH	0.5	1	600	-----	---	-----	200	-----	---	-----	50	-----	AIHA	Yes
Aerozine 50	0.5	1	---	-----	100	-----	---	-----	---	-----	30	-----	NAS/ NRC	Yes
NH ₃	18	25												
CO	50	35												
	50	55												
NO	25	20												
NO ₂	5	9												

exposure by cutaneous absorption, including mucuous membranes and eyes, either by airborne or direct contact with the substance.

The toxicity data presented above represent standards that have been formulated with reference to personnel working with toxic substances, and as such do not represent the only criteria to be considered in evaluating the environmental effects of hydrazine fuel incinerators. Two recent studies have addressed the problem of acceptable atmospheric levels of hydrazine fuels.

The TRW study⁴, which was performed for the Environmental Protection Agency (EPA) and will undoubtedly have a strong influence on future EPA standards, presents a "recommended provisional limit in air" of .01 ppm for N_2H_4 . The basis for this recommendation is given as ".01 times TLV", and presumably this criterion would also be applied to MMH and UDMH. The same set of reports also recommends provisional maximum exposure limits for ammonia (.02 mg/m³), and carbon monoxide (0.55 mg/m³) in air, both values again based on 1 % of the TLV. * It should be mentioned that application of these limits is not entirely straightforward, because of the effects of diffusion, turbulent mixing, distance from the source at which they are to be applied (depending on the location of the source), the possible existence of other sources (particularly in the case of CO), etc.

Another approach was taken by the Environmental Health Office at Vandenberg Air Force Base, which studied all available local and national standards and criteria in formulating the limits presented in Table XII. These limits are taken from Base Reg. 19-1, dated 2 April 1973. Short Term Public Limits (STPL's) are defined as "permissible limits for public exposure during planned release of air contaminants", and Public Emergency Limits (PEL's) are defined as "limits applied to protect the public should an emergency (accident) situation occur". All limits are defined as applying at the perimeter of the controlled area.

⁴Op. cit., Vol. XII, p. 323.

* In the case of ammonia, there appears to be a discrepancy between the stated basis for recommendation and the actual recommended provisional limit.

TABLE XII
CRITERIA FOR PLANNED AND ACCIDENTAL RELEASES

Contaminant	STPL (ppm)					PEL (ppm)		
	10 min	30 min	60 min	5 hr/day 3-4 days/mo	10 min	30 min	60 min	
N_2H_4	15	10	5	2.5	30	20	10	
UDMH	50	25	15	1.0	100	50	30	
NO_2	1	1	1	0.5	5	3	2	

A final consideration in terms of environmental standards is the possible need for relegation to a National Disposal Site. This question was addressed in the TRW report in the following terms:

"Hydrazine does not appear to be a candidate waste stream constituent for National Disposal Sites. It is anticipated that packaged hydrazine and hydrazine in aqueous waste streams will continue to be treated at the source of waste generation. The major products of combustion or decomposition are the elements, water or ammonia which do not present a secondary disposal problem".⁵

Though not specifically mentioned in this report, the same comments can be tacitly assumed to apply to MMH, UDMH, and Aerozine 50.

II. A. 4. Bases for Evaluation

The major products during incineration of hydrazine - type wastes with auxiliary fuels are N_2 , H_2O , CO_2 , and CO formed in varying concentrations depending on thermal and concentration parameters as well as other factors. Minor products of combustion are H_2 , NO_x , C , SO_2 and hydrocarbons. The concentration of NO_x is of prime interest from the environmental and ecological viewpoints.

Table XIII, compiled from available analytical reports,⁶ shows the high and low concentration of combustion products from incineration of N_2H_4 and UDMH.

A study of these reports shows that under optimum conditions only small quantities (5 - 500 ppm) of NO_x pollutant are formed, but up to 10 or 20 times these amounts can form under non-optimum conditions. It also became obvious that the same equipment operating under varying fuel/air ratio, temperature, propellant concentration or type,

⁵ Volume XII, page 335.

⁶ Compilation of data was from the following reports:

- a) Pan Am U327, 3 January 1972
- b) Pan Am MD-EH, 26 February 1971
- c) Pan Am, 8 October 1970
- d) Joel E. Hutson, "Toxic Waste Burner Evaluation", Final Report, AFRPL Contract No. F04611-73-C-0007 (Marquardt Co. Report S-1271), November 1973.

feed rate or other parameters will produce a wide compositional range of the gaseous constituents.

TABLE XIII
CONCENTRATION OF COMBUSTION PRODUCTS

Combustion Product	Incineration of:			
	N_2H_4		UDMH	
	Low	High	Low	High
NO_x , ppm	2	3720	20	4113
CO, ppm	5	19,000	2	76,000
CO_2 , %	0.3	4.4	0.3	9.1
O_2 , %	0.5	18	0.2	20.6
H_2 , %	N. D.	N. D.	.89	12.4
Total HC, ppm	8	N. D.	9.5	1750
HC (As C_g), ppm	< 5	50	< 10	10,700
HC (As CH_4), ppm	< 5	3230	< 10	7000
NH_3 , ppm	6	46	< 0.8	2170
Amines - RNH_2 , ppm	< 5	50	< 4	390
UDMH, ppm	---	---	< 0.5	< 2.0
N_2H_4 , ppm	< .02	30	---	---

The most extensive study that has been performed on incineration of waste hydrazines is the Marquardt study performed for AFRPL.⁷ This was a combined theoretical and experimental study, based on the Marquardt "SUE" (Sudden Expansion) incinerator. The theoretical portion of the study consisted of calculating the theoretical equilibrium compositions of the products of combustion of various combinations of N_2H_4 , UDMH, natural gas, and air. These computations were based on NASA Report SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions,

⁷ Ibid.

Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations", by Sanford Gordon and Bonnie J. McBride, 1971. The results, which of course are not restricted to any particular incinerator design, are presented in Figures 2 through 5.

The experimental portion of the Marquardt program was based on these equilibrium curves, the primary objective being to experimentally verify the more desirable operating points identified by the theoretical results. Results of the experimental program were generally quite satisfactory, giving good agreement with the theoretical predictions and good operating characteristics. The final report stated that

"Using either UDMH or N_2H_4 as the primary fuel and natural gas as an ignition and sustaining fuel, the SUE incinerator ignited easily, burned smoothly, destroyed the primary fuel to less than 2 ppm by weight and produced NO_x at well below the 165 ppm target limit."

The burner used in this test program was an air cooled, 6 inch by 12 inch burner, as shown in Figures 6 and 7. Fuel was injected at the sudden expansion plane and directed toward the centerline of the burner. Combustion began at the sudden expansion and continued downstream for a distance of about two chamber diameters. Waste fuel and natural gas nozzles were typically closed-end tubes with slots near the tips, mounted on circular manifolds at the sudden expansion, although a central poppet nozzle for waste fuel injection was also used in some runs, as shown in Figure 6. Secondary air injection, to obtain complete combustion in the case of fuel-rich primary combustion, and water injection to quench the hot products of combustion and hence minimize NO formation, were also used in some of the tests. Samples were normally taken at the end of the reaction tail pipe, upstream of the scrubber.

Maximum destruction rates were given as 138 gallons per hour for N_2H_4 , 100 gallons per hour for UDMH. These rates were obtained with over-stoichiometric operation, using secondary air injection and water injection to reduce the levels of CO and H_2 in the exhaust. Satisfactory propellant destruction was also obtained at very lean ratios, with acceptable NO_x levels, but in this case destruction rates were very low. Test results,

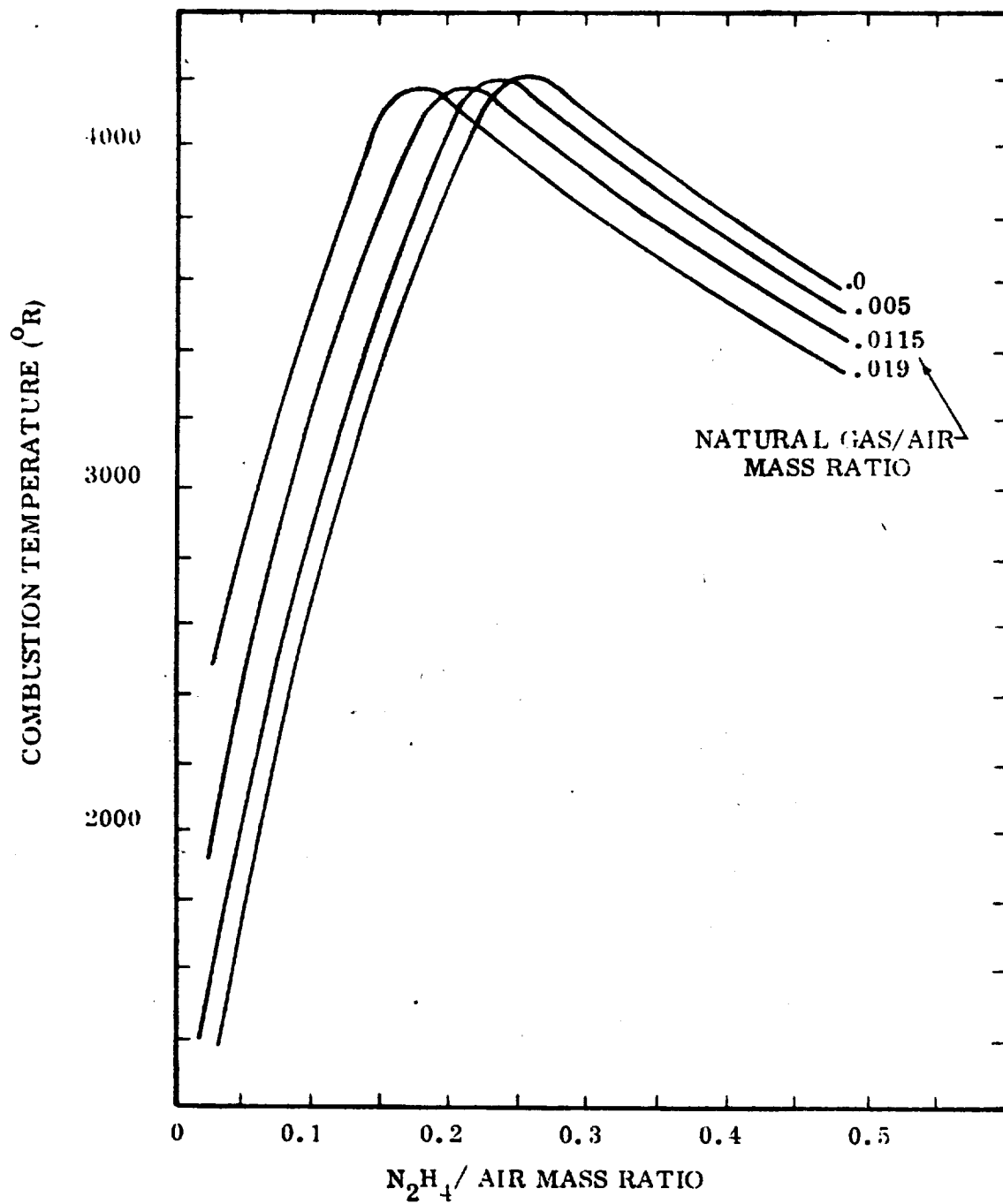


FIGURE 2
ADIABATIC FLAME TEMPERATURES FOR
 N_2H_4 / NATURAL GAS/AIR COMBUSTION
(from Marquardt Co. Report S-1271)

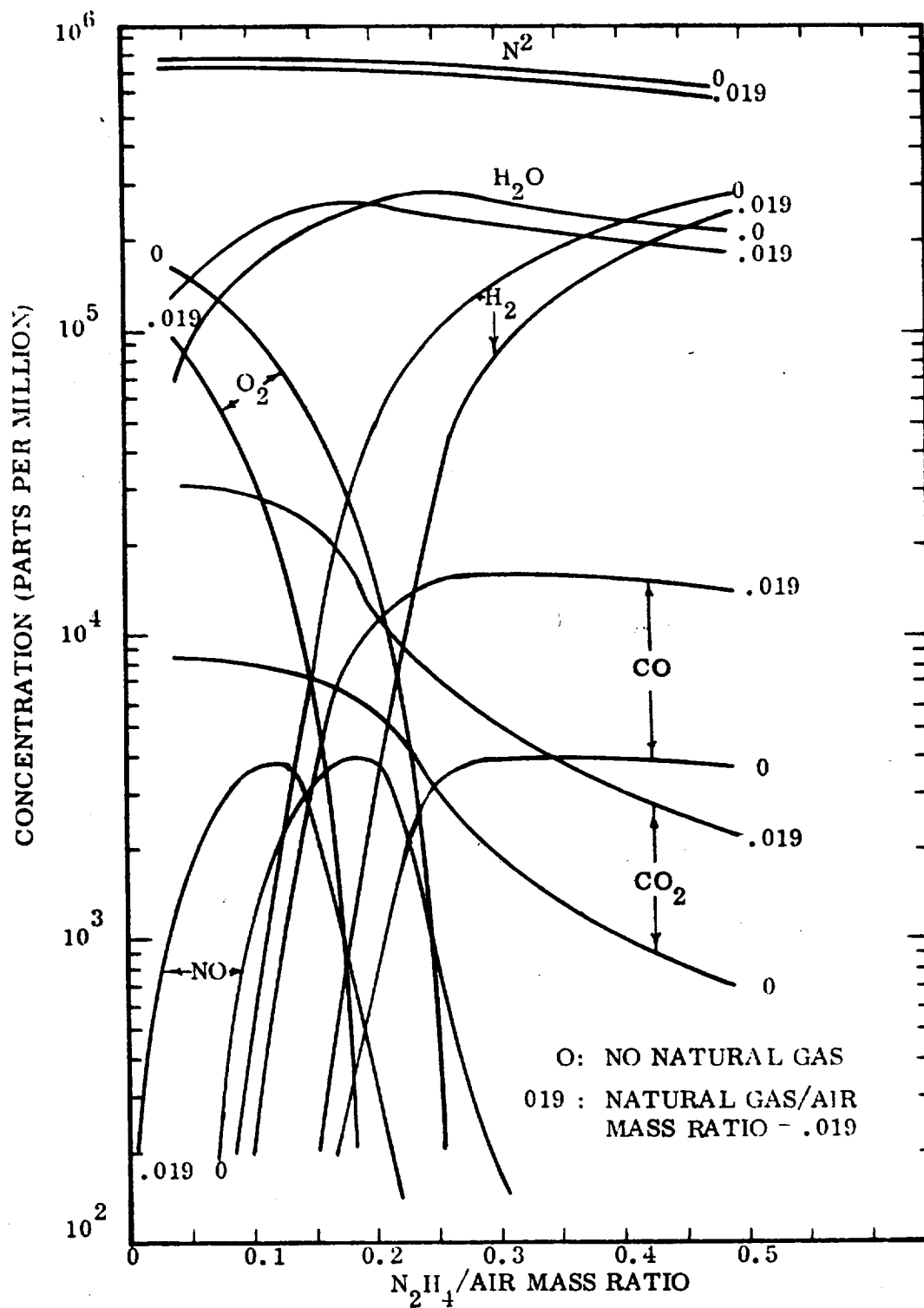


FIGURE 3

THEORETICAL EQUILIBRIUM PRODUCTS FOR
 N_2H_4 /NATURAL GAS/AIR COMBUSTION
 (from Marquardt Co. Report S-1271)

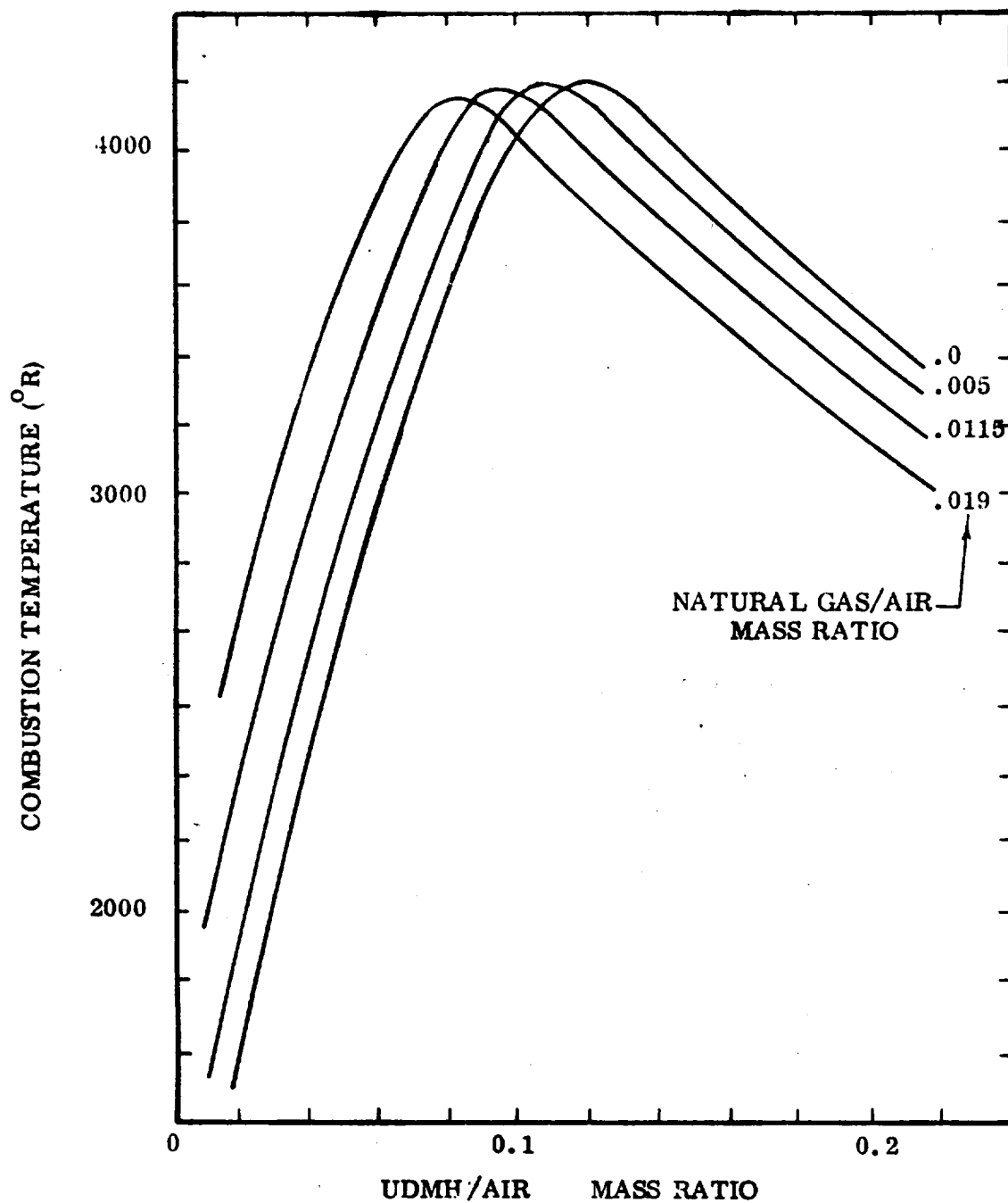


FIGURE 4

ADIABATIC FLAME TEMPERATURES FOR
UDMH/NATURAL GAS/AIR COMBUSTION
(from Marquardt Co. Report S-1271)

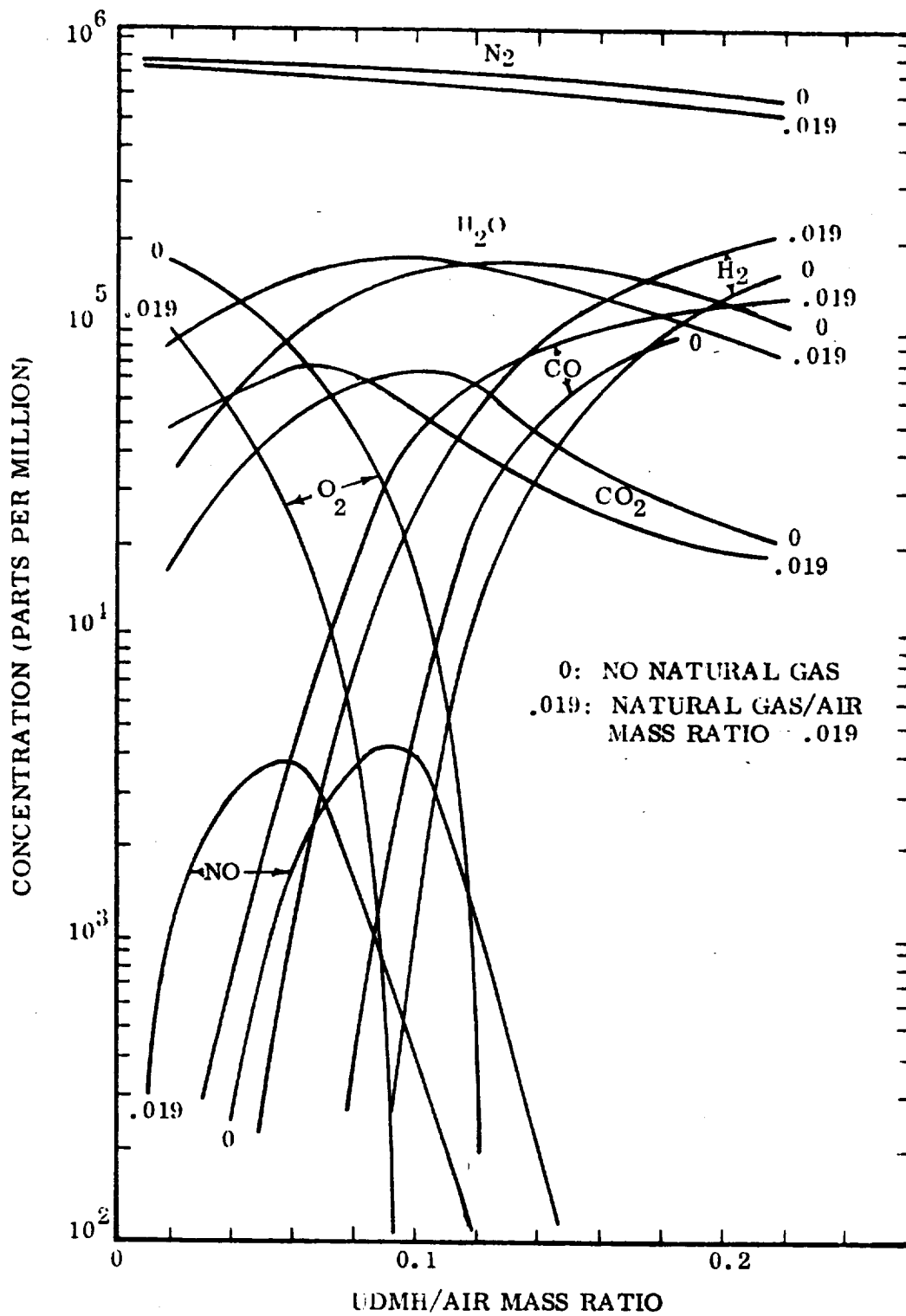


FIGURE 5
 THEORETICAL EQUILIBRIUM PRODUCTS FOR
 UDMH/NATURAL GAS/AIR COMBUSTION
 (from Marquardt Co. Report S-1271)

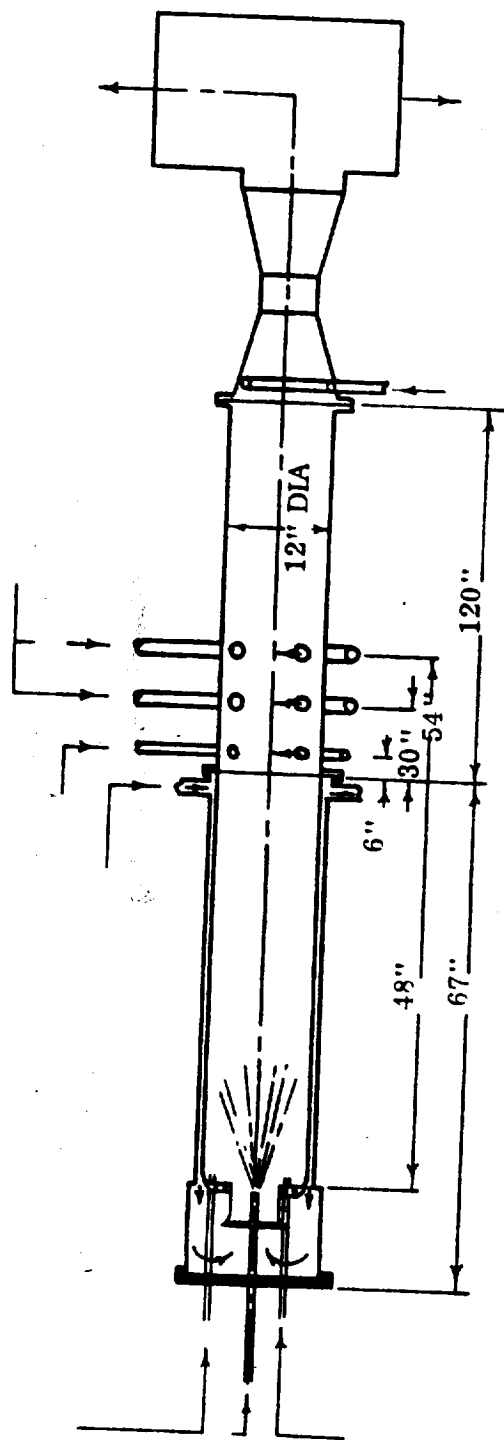


FIGURE 6

N_2H_4 /UDMH "SLE" INCINERATOR, BASIC TEST ARRANGEMENT
(from Marquardt Co. Report S-1271)

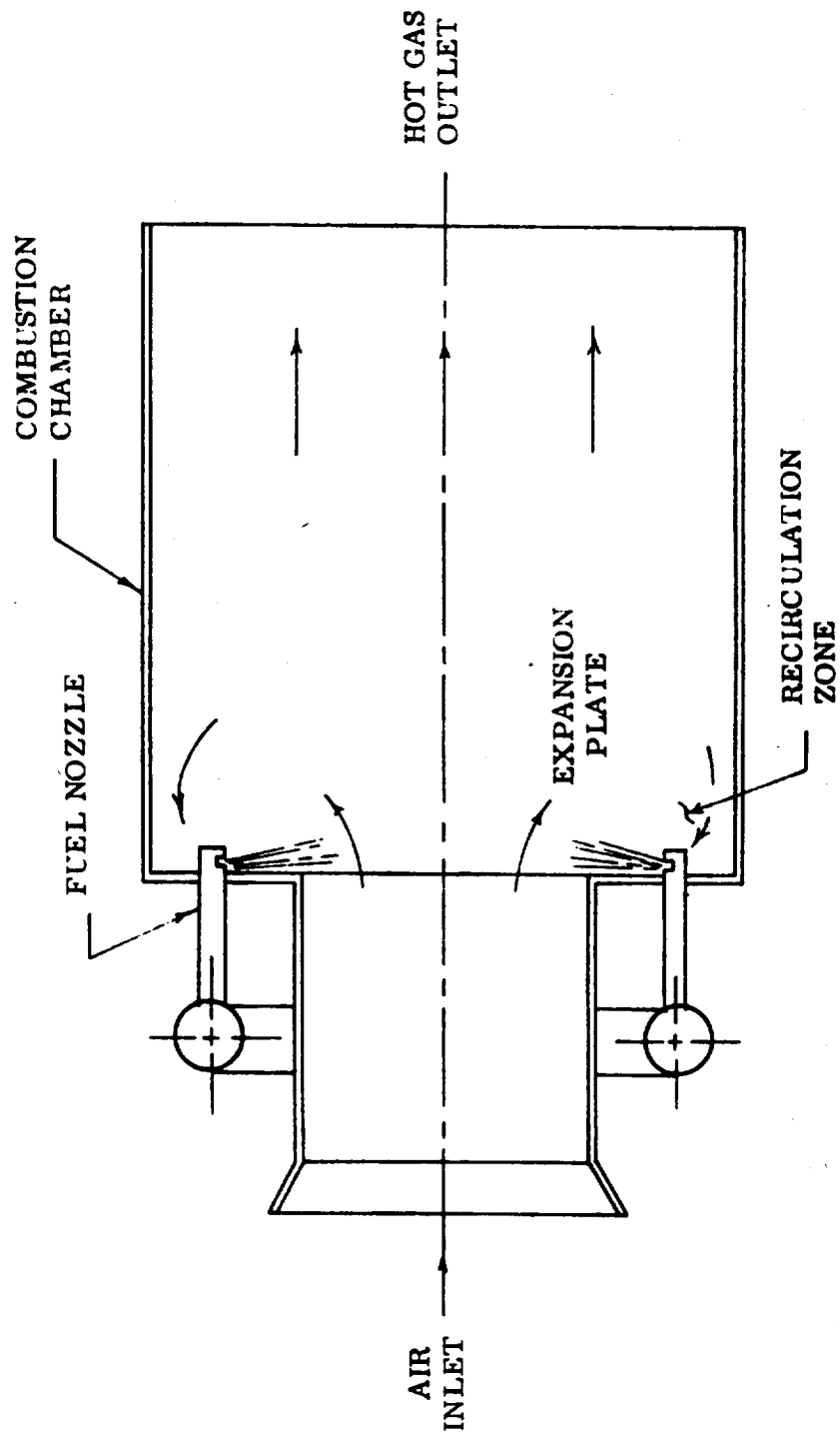


FIGURE 7

TYPICAL "SUE" BURNER CROSS-SECTION
(U.S. Patent No. 3,074,469)

in terms of NO_x measurements, are presented in Figures 8 and 9.

II. A. 5. Overall Evaluation

The data supplied indicate that incineration of hydrazines using an auxiliary fuel (typically liquefied petroleum gas, natural gas, or fuel oil) can be controlled to give environmentally harmless products.

A major difference between some of the various incinerators currently in use involves size and fuel consumption, for comparable waste destruction rates. The overall environmental impact of a large burner with high fuel consumption and long pre-heat periods might be much more adverse than considerations of trace species concentrations in the effluent would indicate.

The only example we have seen of a small, modern incinerator that is well-adapted to on-site, quick-reaction disposal of hypergolic propellants is the "SUE" (SUdden Expansion) incinerator marketed by the Marquardt Company, Van Nuys, California. In the program described in the preceding section, this incinerator was tested and evaluated as a means of disposing of N_2H_4 , UDMH, and N_2O_4 . Although the N_2O_4 tests were inconclusive, the N_2H_4 and UDMH tests gave quite satisfactory results, and there is no reason to believe that the same incinerator wouldn't be equally effective for MMH.

Maximum acceptable propellant mass flow rate through this burner is 138 gallons per hour for N_2H_4 , 100 gallons per hour for UDMH, with a natural gas flow of .008 and .012 pounds per second, respectively, or approximately 700 and 1000 SCFH. At these flow rates, 5000 gallons of waste fuel could be destroyed in 36-50 hours of continuous operation, or a 55-gallon drum in a half hour or so. Because of the use of natural gas as an auxiliary fuel, there need be no minimum flow rate of the waste propellant. Warm-up time (required to stabilize the flame, etc.) is five to ten minutes. For these reasons, we believe this incinerator is an acceptable disposal method for liquid hydrazines in both large and small quantities.

As a practical matter, it would be desirable if the same incinerator

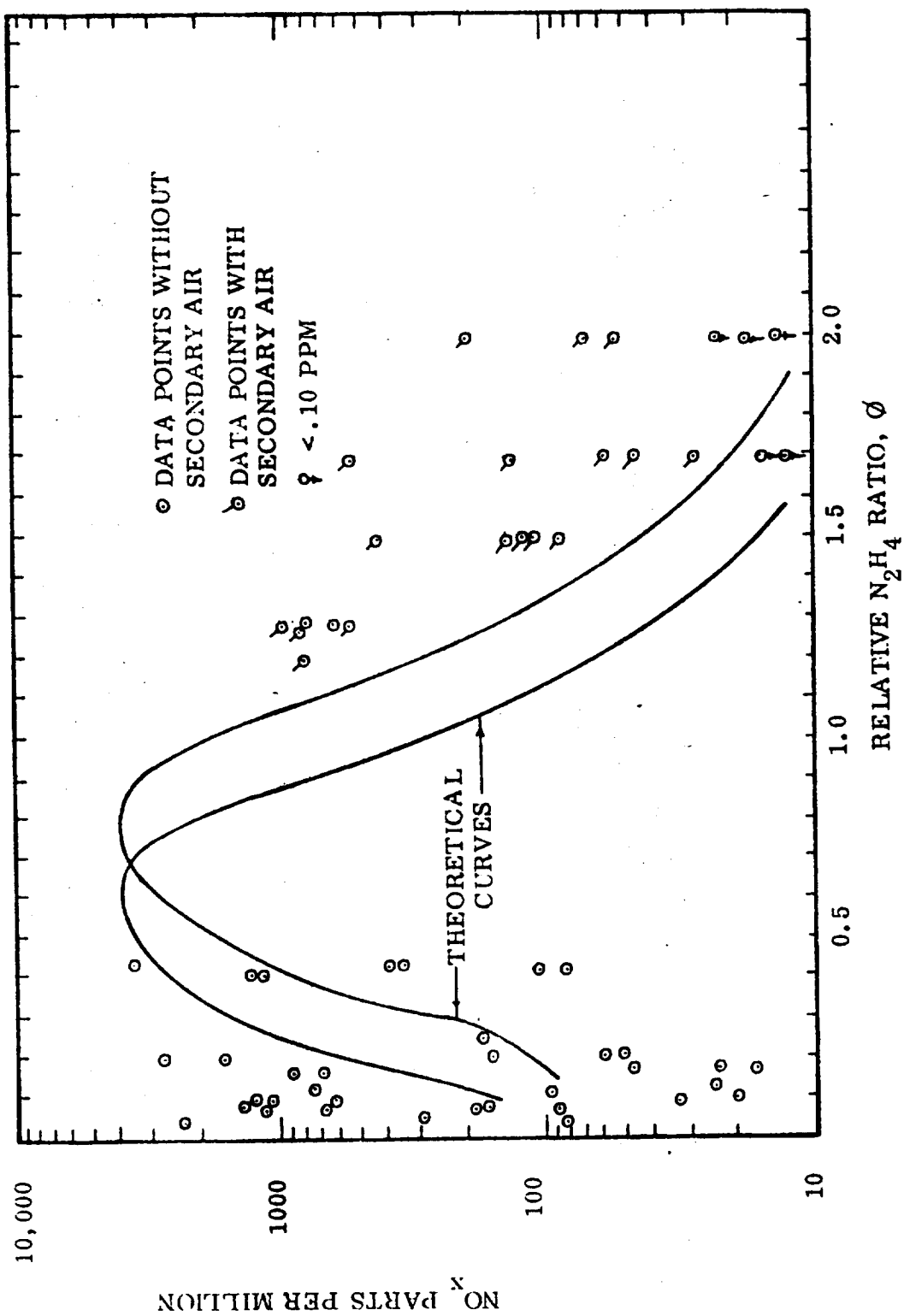


FIGURE 3

TOXIC WASTE PROGRAM TEST RESULTS: NO_x EMISSION FROM
 N₂H₄/AIR/NATURAL GAS COMBUSTION
 (from Marquardt Co. Report S-1271)

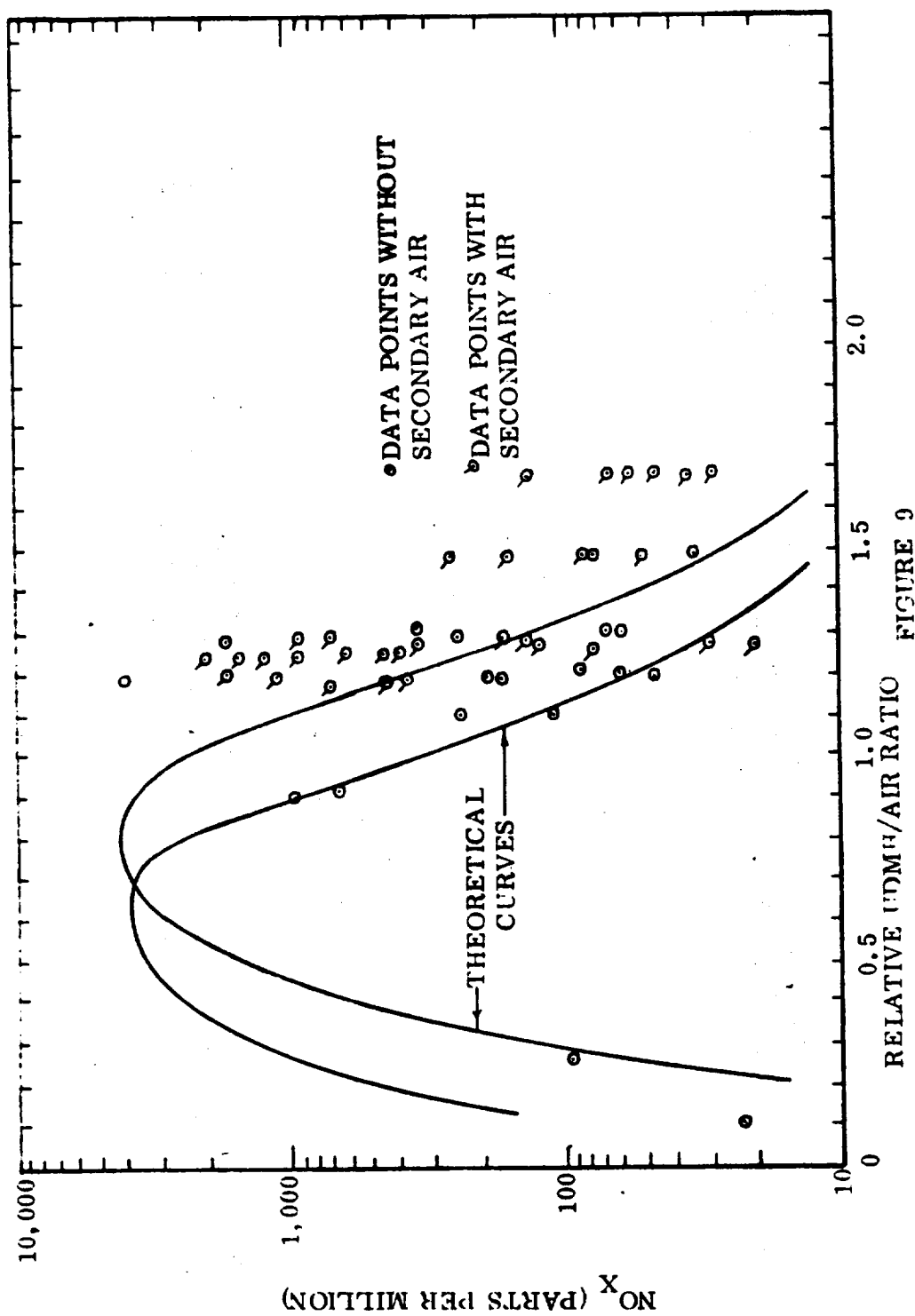


FIGURE 9

TOXIC WASTE PROGRAM TEST RESULTS: NO_x EMISSION FROM
UDMH/AIR/NATURAL GAS COMBUSTION
(from Marquardt Co. Report S-1271)

could be used for disposal of both liquid hydrazines and hydrazine vapors. We believe there is a good possibility that the SUE incinerator could be adapted to this multi-mode operation, but that this modification would require a development and test program to establish its effectiveness.

Other development work might also be beneficial, and Marquardt's final contract report mentions that a desirable modification might be a longer reaction tailpipe, with a turbulator section, to more effectively reduce CO and CH_x emissions when operating over-stoichiometric with secondary air injection.

Other incinerators might also be developed that would be at least equally effective. While the SUE burner is modern and well-designed by comparison with the large units installed at various sites during the early 1960's, it is not very advanced in terms of current combustor technology, particularly with regard to nozzle design and secondary air injection.

Our overall evaluation, however, is that the SUE burner is currently an environmentally acceptable means of destroying liquid hydrazine fuels. Large incinerators of the type still in use at ETR are also environmentally acceptable in terms of point-of-use emissions, on the basis of the Pan American World Airways data included in Table XIII, and other unpublished data. The overall environmental impact of these larger units might be judged unfavorable on the basis of their very high consumption of hydrocarbon fuels, however. In addition, their more complex operational requirements, special siting requirements, and long warm-up cycles all place them at a disadvantage compared to the smaller, simpler SUE burner, and we have not been able to identify any grounds on which their performance is superior to that of the SUE unit, except for the ability to destroy aqueous solutions. At the same time, we believe that the SUE in its current form does not represent a very advanced level of combustor technology, and that further development of either the SUE concept or other concepts could yield substantial improvements in the future.

B. OPEN PIT INCINERATION

II. B. 1. Current Applications

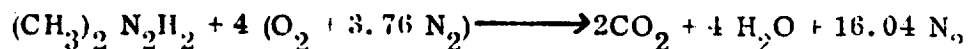
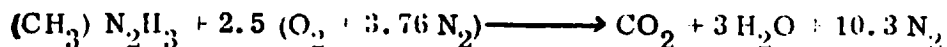
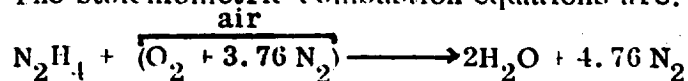
Open pit burning is recommended by the chemical industry for disposal of large quantities of hydrazines, and is still in fairly widespread use, although it seems to be less prevalent now than several years ago. The TRW study¹ labeled this method "generally acceptable" but warned of excessive NO_x generation. Concentrations less than 40% are not combustible, and other contaminants might also pose a problem.

II. B. 2. Thermochemical Aspects

An open pit incinerator consists of a rigid shell or lined pit of suitable width and height with an open top. An array of closely spaced nozzles might be used to provide high velocity air over the burning zone.

High burning rates, long residence time, and high flame temperature are achieved. Smoke can be controlled but some particulate matter (soot) and a visible plume of toxic gas (NO₂) is produced. Exit gases are released directly to the atmosphere.

The stoichiometric combustion equations are:



It must be emphasized that mixture ratios and temperatures are not well controlled in this process, and can vary substantially with both position and time. Formation of partial products and oxides of nitrogen is to be expected. The usual means of minimizing these emissions do not seem applicable to open pit burning.

¹Op. cit., Vol. XII, page 333.

II. B. 3. Environmental Standards

All products of combustion are released directly to the atmosphere, and hence environmental standards are those detailed in the preceding section on incineration.

II. B. 4. Overall Evaluation

Although open pit incineration is an effective means of destroying hydrazines, the probability of excessive generation of oxides of nitrogen, and CO in the case of the methyl-substituted hydrazines, render it environmentally undesirable, in our view. The TRW report² comments that "For drum quantities of hydrazine this method is generally acceptable although since excessive NO_x might be generated another option would be preferred". Because of the number of other options available, and their overall acceptability, we prefer to regard open pit burning as unacceptable for the purposes of this study, except under certain special circumstances such as emergency situations in remote locations.

C. CHEMICAL TREATMENTS

II. C. 1. Current Applications

A number of the organizations contacted in Phase I of this study dispose of hydrazines by dilution followed by neutralization. The chemical industry recommends neutralization using calcium hypochlorite or a dilute solution of hydrogen peroxide, catalyzed by a trace amount of copper sulfate. Dilute hydrochloric or sulfuric acid is also recommended in the case of MMH, and atmospheric oxygen in the presence of copper salts for N₂H₄.

The catalyzed hydrogen peroxide reaction is currently being used by several of the organizations contacted, but not, as far as we could ascertain, the hydrochloric or sulfuric acid reactions. Two organizations precede the hydrogen peroxide reaction with addition of sodium hydroxide, and at least one uses sodium hydroxide alone to treat dilute hydrazine wastes. Also used for neutralization purposes are dilute nitrogen tetroxide,

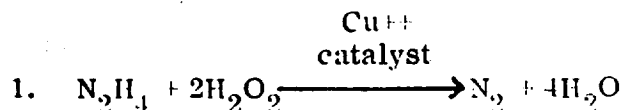
²Ibid.

sodium hypochlorite, and hydroxyacetic acid. (Nitrogen tetroxide is often used in a de facto manner simply because the same holding ponds are used for both fuel and oxidizer wastes.)

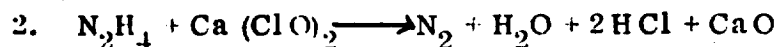
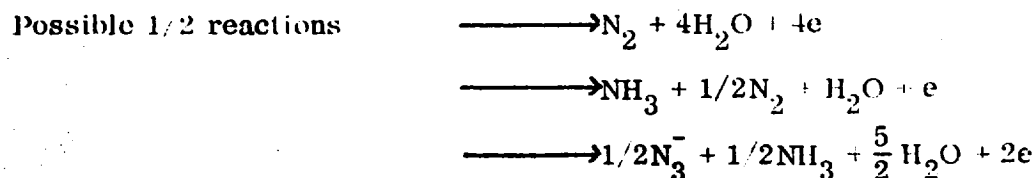
Hydrazine vapors are often sent through water-spray scrubbers, and the water then treated by one of these neutralization reactions.

II. C. 2. Chemical Description

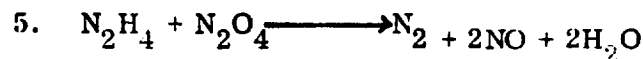
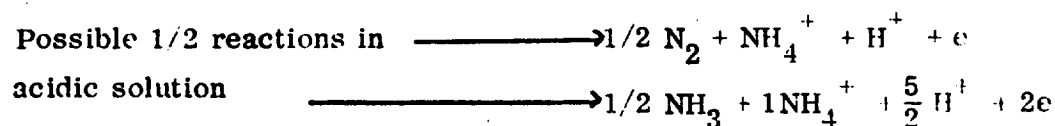
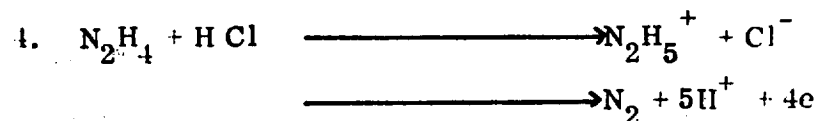
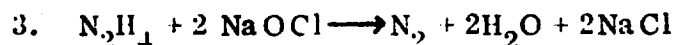
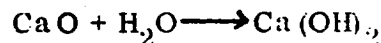
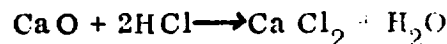
Equations show reactions in dilute solutions, for N_2H_4 :



In basic solution N_2H_4 acts as a reducing agent:

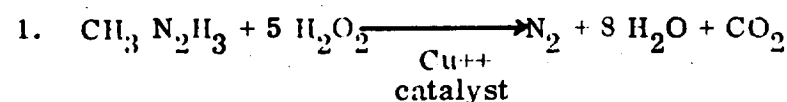


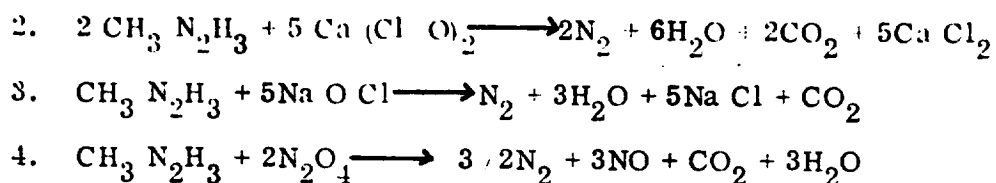
In solution CaO reacts:



6. NaOH is used primarily to adjust the pH of the solution, and does not react with the hydrazine to any significant extent.

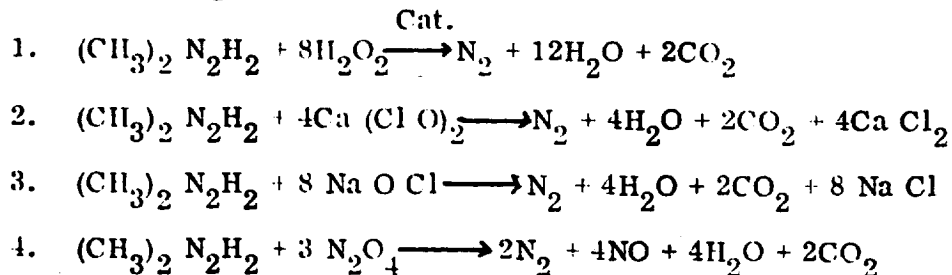
The comparable reactions for MMH are:





These equations are idealized for complete reaction. As in most chemical reactions trace amounts of possible products formed are not shown.

The same reagents react with UDMH as follows:



Small quantities of hydrazine-type fuels collected into a sump, tank or pond are highly diluted with H_2O (at least 1:100). The pH is adjusted and catalyst added, if required. The solution is then treated with one of the reagents given in the equations above and in Table XIV. These reagents are applied slowly and in slight excess to allow heat dissipation from the reaction. The treated solution, checked for pH and presence of amines, is discharged into a stream, sewer or ground surface possibly with additional dilution.

Heat is generated in quantity in each of the reactions so that controlled addition of reagent is necessary. Some means is required for insuring complete decomposition of propellant during treatment without excessive addition of reagent thus adding to the overall cost.

The figures for the reagent cost were derived from recent prices of ton lots of the reagent in the amount required for the stoichiometric neutralization of the propellant. Although the reagent costs were computed, these values were not used for final evaluation since they may be overshadowed by other factors.

Hydroxyacetic acid was not included in Table XIV due to its excessively high cost (\$3.75/kg for 70%) and to the fact that only one company mentioned its use several years back (early Apollo flights).

II. C. 3. Environmental Standards

Any vapors reaching the atmosphere from neutralization ponds would be governed by the standards detailed in Section A above, "Incineration". Primary effluent from any neutralization pond, however, is a liquid release, and in this case environmental standards are much less well defined.

The closest approximation we found to published standards regarding allowable hydrazine levels in water or soil are the recommendations of the TRW report referred to several times in earlier sections of this report. The TRW study, as stated earlier, was funded by EPA and probably represents an important part of the basis for future EPA standards. The TRW report³ recommends a provisional limit of 1.0 ppm hydrazine in water and soil, giving as their "Basis for Recommendation" the statement that "Quantity will rapidly oxidize to near-zero concentration".

The TRW report also recommends provisional limits⁴ for several of the other constituents that might appear in neutralization pond effluents, as shown in Table XV.

II. C. 4. Bases for Evaluation

The recommended provisional limits in the preceding sub-section are obviously very low, and in fact the limits for all of the neutralization reagents listed in Table XIV, as well as reaction products such as slaked lime and quicklime, are actually much lower than the limit for hydrazine itself. We must therefore conclude that if any of these reagents is to be used, quantities must be very carefully controlled and concentrations continuously monitored to avoid excess reagent addition. Since these reagents are all water soluble, excess addition will result in the reagent appearing in the pond effluent.

The safety factors involved in handling these reagents is an important consideration in evaluation. For this reason, hydrogen peroxide possesses special advantages in that since it is already present at KSC and used as a hypergol, its use in neutralizing the hydrazines would obviate the need to employ other agents with different safety properties which physicians and workers would have to be alerted to.

TABLE XIV

NEUTRALIZING REAGENTS FOR HYDRAZINE FUELS

Method	Neutralizing Reagent	Products Formed	Comments		Pollution
			Safe Operation, Effluent Inconspicuousness	Chemical Cost per lb fuel	
1	H_2O_2	N_2, H_2O + trace NH_4 salts	1 Heat generated, rate of Chemical addition should be controlled. 2 Inconspicuous	\$1.15 (N_2H_4) \$2.00 (MMH) \$2.45 (UDMH)	Present in effluent: Na^+ salts, trace Fe^{3+} or Cu^{++} and NH_4^+ salt
2	$Ca(ClO)_2$	N_2, H_2O Ca^{++} salts	1 " 2 "	\$1.58 (N_2H_4) \$2.75 (MMH) \$3.37 (UDMH)	Ca^{++} salts, Cl^-
3	$NaOCl$	N_2, H_2O NH_4^+ salts	1 " 2 "	\$1.49 (N_2H_4) \$2.59 (MMH) \$3.18 (UDMH)	Na^+ salts, Cl^-
4	HCl	N_2, H_2O NH_4^+ salts	1 " 2 "	\$0.24 (N_2H_4)	Cl^- , NH_4^+ salts
5	N_2O_4	N_2, NO H_2O	1 " 2 "	(see discussion for cost)	NO release to air or HNO_2 , HNO_3 in H_2O . NO gives secondary pollution problem.

TABLE XV
RECOMMENDED PROVISIONAL LIMITS FOR
POSSIBLE NEUTRALIZATION POND EFFLUENT CONSTITUENTS,
from TRW Report No. 21485-6013-RU-00

Contaminant in Water and Soil	Provisional Limit	Basis for Recommendation
Calcium hydroxide (slaked lime)	0.25 ppm	Stokinger and Woodward Method
Calcium oxide (quicklime)	0.25 ppm	Stokinger and Woodward Method
Ammonium hydroxide (ammonia water)	0.01 ppm	Stokinger and Woodward Method
Hydrochloric acid	0.35 ppm	Stokinger and Woodward Method
Hydrogen peroxide	0.07 ppm	Stokinger and Woodward Method
Mixed acid	0.05 to 0.25 ppm	Stokinger and Woodward Method
Nitric acid	0.25 ppm	Stokinger and Woodward Method
Sulfuric acid	0.05 ppm	Stokinger and Woodward Method
Sodium hypochlorite- Na OCl	0.10 ppm	Stokinger and Woodward Method
Calcium hypochlorite- Ca (ClO) ₂	0.125 ppm	Stokinger and Woodward Method
Hydrazine- N ₂ H ₄	1.0 ppm	Quantity will rapidly oxidize to near-zero concentration

Even more severe than the restriction on neutralization reagents in the effluent, however, is the restriction on ammonium hydroxide, or ammonia gas dissolved in water. If this restriction is incorporated in future liquid waste discharge standards, it would be a strong factor against the selection of those reagents (H_2O_2 , HCl) that result in the formation of ammonia gas and ammonium radicals.

The liquid effluents from these systems will also contain ions of Ca^{++} , Na^+ , Cl^- , NO_2^- , or NO_3^- . These materials can be released in small quantities into a sewer, stream or ground without undue concern for the present pollution regulation.

Selection of a ground waste disposal site should be based so that the discharged liquid waste infiltrates and percolates into the ground surface where no possibility of impairment exists. Disposal of wastes should not be near fresh water aquifers, wells or any other usable water sources.

All of these disposal methods will meet the air pollution standards since N_2 is the only gas released. The NO formed in reaction 5 will dissolve in H_2O forming HNO_2 when sufficient H_2O is available, as is usually the case.

II. C. 5. Overall Evaluation

Because of the overall controllability of neutralization ponds - the fact that, with adequate capacity, unplanned releases need not occur, and effluent discharge can await "satisfactory" conditions within the pond - and because of the absence of air pollution factors, it is our conclusion that neutralization ponds using any of the reagents listed in Sub-Section 2 are environmentally acceptable as means of destroying hydrazine fuels. This acceptability is of course dependent on the provision of adequate equipment and procedures for monitoring and controlling the composition of the pond. It might also be necessary in some cases to provide a means of secondary dilution, such as a separate discharge pond.

Acceptability does not imply practicality, however, and we believe that the practicality of these neutralization systems is very dependent on the severity of future restrictions on ground water discharges. As long as reasonable amounts of dissolved hypochlorites, and slaked lime and quicklime, are allowed, methods 2 and 3 in the tables are practical, although somewhat expensive. If dissolved ammonia is also allowed in small quantities, the H_2O_2 system would also be quite practical, and if very dilute HCl can also be discharged, the low chemical cost of this reagent could make it quite attractive. Use of N_2O_4 (other than diluted waste N_2O_4) is not advocated primarily due to the unpredictable logistics and costly adequate control problems. On an assumed cost of \$.25/lb of N_2O_4 , the chemical cost to treat 1 lb N_2H_4 would be \$0.72.

Our first choice among the listed reagents, keeping in mind possible operational complications as a result of future environmental standards, would be hydrogen peroxide. Its use as a hypergol means that it will always be available at KSC. Thus involved personnel will not have to familiarize themselves with the safety properties of another agent. Also, as seen in Table XIV, H_2O_2 can neutralize the hydrazine at less cost than the hypochlorites.

It should be mentioned that the possibility of using the same neutralization pond for both fuel and oxidizer destruction is a significant factor in evaluating the desirability of these disposal systems for specific applications. Another attractive feature is the fact that large quantities of either fuel or oxidizer could be very quickly transferred to a neutralization pond in emergency situations, whereas incinerators have inherent flow rate limitations.

D. DILUTION AIR OXIDATION/BACTERIAL ACTION

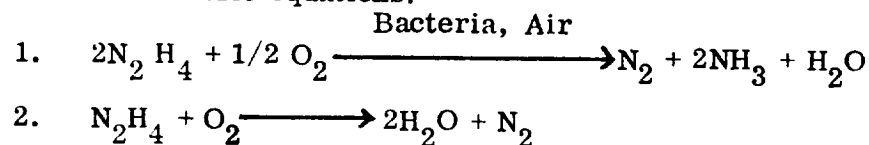
II. D. 1. Current Applications

Water dilution of liquid hydrazine wastes followed by discharge to untreated holding ponds is one of the most common means of disposal of this fuel. In the holding pond, air oxidation and bacterial action slowly convert the hydrazine to nitrogen, ammonia and water, as described in the following subsection. In some operations, normal evaporation is sufficient to control the holding pond level and liquid is never withdrawn from the holding pond.

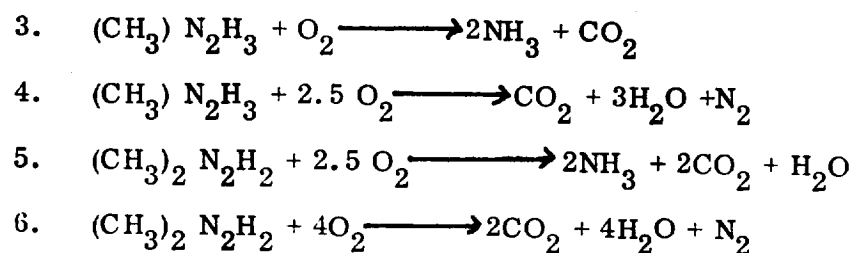
Aeration - either by bubbling air through the pond, or by spraying pond water up into the air - is a variation on the air oxidation approach that will speed up the destruction of hydrazine by making oxygen more readily available to all parts of the pond. Air bubbling was found in Phase 1 of this study to be in use at two locations at the present time, and a spray pond is currently being tested at Vandenberg Air Force Base.

II. D. 2. Chemical Description

Hydrazine fuel is mixed with copious amounts of water to form a very dilute hydrazine solution, in which hydrazine slowly decomposes - aided by bacterial action - and reacts with dissolved oxygen according to the following two stoichiometric equations:



The equations for MMH and UDMH are:



The primary function of air bubbling, or water spraying, is to improve on the quiescent situation, in which oxygen is available only at the surface, by distributing oxygen through all parts of the pond - or, in the case of sprays, by distributing all parts of the pond through the oxygen. In any case, the oxidation reaction is very slow at atmospheric temperature, and the heat release in a pond will not significantly raise the temperature such as to increase the rate of reaction. (Unlike the case of air oxidation of anhydrous hydrazine in a confined area, which can be unstable and result in fire or explosion.)

In normal sewage treatment practice, an oxidation pond utilizes bacteria to aerobically stabilize the organic material present in the waste water, resulting in the conversion of C to CO_2 , H_2 to H_2O , and N_2 to NH_3 . The oxygen for the bacteria is supplied by both air surface transfer and the metabolism of algae in the pond. The cycle is completed when the algae use the waste stabilization products CO_2 and NH_3 to synthesize new cells in the presence of sunlight, and thereby liberate oxygen as an end product to be used by the bacteria for oxidizing the organic wastes and synthesizing bacterial protoplasm. In addition to biological stabilization, other processes taking place in oxidation ponds may include balancing of the acids, coagulation and sedimentation of solids, and neutralization of any alkalinity.

II. D. 3. Environmental Standards

Environmental standards are the same as those outlined in the preceding section on neutralization ponds.

Visits by study personnel were made to the Western Test Range at Vandenberg Air Force Base, Johnson Space Center, and White Sands Proving Ground to observe existing oxidation ponds first hand and talk with engineers responsible for their design, maintenance and operation. The only operational aeration pond was at Johnson Space Center, where a very large flow of air is introduced through two H-shaped manifolds at the bottom of a fairly deep concrete holding pond. The bubbles generated are quite large, and result in a general roiling motion of the central part of the pond and visible circulation throughout

most of the pond. At the Western Test Range, a spray pond has been constructed for experimental purposes, and one batch of hydrazine has been oxidized in the pond for data collection purposes. Oxidation ponds at White Sands Proving Ground are essentially untreated holding ponds, with air oxidation taking place naturally at the surface but no aeration.

Measurements at both Western Test Range and Johnson Space Center show that during aeration a period of time passes in which dissolved oxygen levels in the water increase, but there is no significant reduction in hydrazine level; this period is followed by a reduction in hydrazine content once the dissolved oxygen reaches saturation.

Operating experience at the one operational holding pond has apparently been quite satisfactory. It should be noted, however, that very little hydrazine disposal has taken place at JSC during the time (several months) that the aerator has been installed in this pond. The primary reason for installation was to provide a means of quickly oxidizing the hydrazine in case of emergencies - the need for pumping water from the pond to prevent overflow during very rainy weather, for example. Starting with a 300 ppm N_2H_4 concentration in 0.5 million gallons of water, the hydrazine concentration can be reduced to 5 ppm in about twenty hours, with most of the reduction occurring in the last two to three hours. The addition of copper sulfate or iron oxide as a catalyst contributes to the speed of oxidation.

In the experiment at WTR, mixed hydrazine fuels were added to 50,000 gallons of water to a level of 120 ppm, with 0.2 mg/l copper ion as catalyst. The mixture was then sprayed into the air at a rate of 60 liters per minute for eleven days, achieving dissolved oxygen saturation, and allowed to sit. The hydrazine disappeared slowly thereafter, with oxidation essentially complete after another nine days. There was no significant emission to the atmosphere - only trace amounts of UDMH could be detected at a point six inches above the pond surface, except for one 6 ppm reading made thirty minutes after hydrazine transfer to the pond.

The only undesirable end product identified by the stoichiometric equations is ammonia, which will be dissolved in the water (ammonium hydroxide) and released to the atmosphere to some extent. The threshold Limit Value for ammonia in air recommended by the American Conference of Governmental Industrial Hygienists is 25 mg/m^3 , and the provisional Maximum Exposure Limit recommended by the TRW Study¹ is $.02 \text{ mg/m}^3$. Actual levels above oxidation ponds are difficult to calculate because of undetermined effects of numerous variables such as insolation (intensity, hours per day, etc.), bacterial action, surface area versus depth, temperature, relative humidity, wind velocities, etc. In view of the slow rates involved with oxidation pond processes, and the absence of reports of ammonia odors, we see no reason to expect atmospheric ammonia releases to be a problem except perhaps in the case of spray ponds.

In many applications, it would be expected that periodic liquid discharges from oxidation ponds would be required. In these cases, the ammonia content of the water could be a problem, especially if the very restrictive ammonium hydroxide provisional limit shown in Table XV is adopted. In addition, because of the slowness of the air oxidation reaction, two ponds (probably in series) would have to be used so that the pond being emptied could be protected from fresh hydrazine addition for a period of time prior to discharge.

Selection of a ground waste disposal site should be such that the discharged waste infiltrates and percolates into the ground surface where no possibility of impairment exists. Disposal of wastes should not be near fresh water aquifers, wells, or other usable water sources.

¹Op. cit., Vol XII, pages 102-104.

II. D. 5. Overall Evaluation

Provided that the various restrictions of the preceding subsection are met, it is our conclusion that an oxidation pond is an acceptable means of destroying waste liquid hydrazines. Indeed, it is one of the most acceptable means, as it possesses most of the advantages of the neutralization ponds without the disadvantage of introducing other chemicals, possibly harmful to the environment, into the process. An additional advantage is the fact that, since salts and other dissolved solids are not formed, there is no inherent necessity for periodically draining the pond. As long as the hydrazine addition does not exceed the capacity of the pond, there is no reason why it cannot continue to function indefinitely, with the only effluents being nitrogen, water vapor (normal evaporation) and trace amounts of ammonia into the atmosphere.

The entire question of aeration ponds was investigated in greater depth during Phase 3, including the use of an ozone generator to add this strong oxidizer to the gas bubbled into the pond. Results of these studies are included in the sections on Alternate Disposal Concepts and Application Studies.

E. OPEN BURNING

Open burning is the burning of waste material on open land without the use of combustion equipment. This method is not used frequently for propellant destruction. Generally, considerable black smoke along with NO_x and CO are evolved to the atmosphere. These emissions are the result of uncontrolled combustion temperature, incomplete combustion due to poor gas mixing with air, and insufficient residence time of the generated particulate at elevated temperature.

Open burning is not considered to be an adequate form of waste propellant disposal because of associated loss of gaseous effluent control.

F. OCEAN DUMPING

Ocean dumping of a wide variety of hazardous wastes, including propellants, has been carried out by many nations as an expedient or an economically attractive disposal technique. Sea water is used as a reactant or neutralizing medium and as a diluent.

The Council on Environmental Quality recommended "To ban unregulated ocean dumping of all materials, and strictly limit ocean disposal of any materials harmful to the marine environment". In response, in October 1970, President Nixon recommended legislation to stop ocean dumping.

Several bills now in the House would totally ban ocean dumping of any toxic industrial waste, radiological waste or waste matter from chemical or biological warfare material. As a result it can be expected that more restrictive standards will be imposed in the future. It is for these reasons that ocean dumping was deemed environmentally unsound and was not pursued in this study.

G. POURING DIRECTLY ON OPEN GROUND

Informal communications and conversations have indicated that the pouring of waste liquid hydrazines directly on the ground in remote areas is still occasionally practiced, in an informal and unpublicized manner. Certainly it would be difficult for us to make a strong case regarding the undesirability of disposing of minute amounts in this fashion. Hydrazine is not a "persistent" chemical, and will rapidly oxidize to near-zero concentration, as pointed out in the TRW report.¹

As a means of disposing of any significant amount of waste fuel, however, this method certainly cannot be recommended. In addition to the danger involved in actually carrying out the operation, there is the likelihood

¹Op. cit., Vol XIII, page 333.

of uncontrolled vapor release, and unpredictable local effects, including possible lingering contamination in the case of significant quantities of hydrazine.

III. DISPOSAL OF HYDRAZINE VAPORS

A. INCINERATION

III. A. 1. Current Applications

Only one organization was found during Phase 1 of this study to have the capability of destroying hydrazine vapors by incineration, and this organization's systems are used primarily for products of combustion (or dissociation) rather than directly for hydrazine.

These systems are used in conjunction with testing of small hydrazine gas generators and APU's. Exhaust from the test cells is carried to small rooftop incinerators - essentially 55 gallon drums with equipment panels at one end and exhaust deflectors at the other. Natural gas is fed through the equipment panel, which also includes a squirrel cage blower and a spark plug. The air and gas are mixed, and ignition is initiated by the spark plug. The flame enters the drum through a central hole in the fire-brick lining on the end; the waste (exhaust) gas from the test cells is fed into the flame in the central part of the drum by means of a downstream facing duct. The unit is fired prior to the beginning of a test in the cell below it. These units were installed after hydrazine testing began, in order to eliminate a problem with ammonia odors in the test buildings, and they have been quite successful.

In addition to the rooftop units there is a large incinerator, originally manufactured by Hirt Combustion Engineers, that services the test facility. Deluge water from the cells is drained to a sump adjacent to this incinerator; when enough accumulates, the incinerator is fired and the contents of the sump injected into it. In addition, there are 6" lines coming directly to the incinerator, through a liquid-vapor separator in the sumps, from two of the test cells for exhaust gas from engines running in those two cells.

Both liquid and vapor can be fed to the incinerator simultaneously. Natural gas and waste vapors are injected into the main air stream through an array of nozzles, and the liquid is sprayed into the flame region through a central nozzle. The sump pump, which supplies liquid to this central nozzle, can draw either from the sump, from the liquid-vapor separator, or from a small external tank that can be used to dispose of contaminated propellants directly. In case of flame-out, the sump pump is shut off, and a burst disc directs the waste gas flow to the bottom of the sump, where it bubbles through the sump water to atmosphere.

With the exception of this system, which has apparently not been used for the destruction of actual hydrazine vapors (as opposed to dissociation products), we know of no applications in which hydrazine-containing vent gases are fed to any sort of incinerator, combustion chamber, or flare burner.

III. A. 2. Thermochemical Aspects

The discussion of thermochemical aspects presented in Section IIA, Incineration of Liquid Hydrazines, applies equally well to the incineration of hydrazine vapors. From the point of view of combustion, the only difference between liquid and vapor is the difference in enthalpy (latent heat), which will have a slight effect on flame temperature (higher in the case of vapor).

Another difference does exist, however, in that it is not expected that pure hydrazine vapors will normally be encountered in any disposal system. Since the hydrazines are normally liquid at standard atmospheric conditions, their vapors can only exist in mixtures containing noncondensable gases. The vapor pressures of N_2H_4 , MMH, and UDMH at 25 C are given in Table XVI. The mole fraction of any constituent in a mixture of perfect gases is equal to the ratio of its partial pressure to the mixture pressure, and in equilibrium the partial pressure cannot exceed the vapor pressure corresponding to the temperature of the mixture. The maximum, or saturation, mole fractions for hydrazine vapors mixed with other gases at standard atmospheric conditions are also given in Table XVI. Saturation mass fractions,

TABLE XVI
LIQUID-VAPOR SATURATION PROPERTIES OF HYDRAZINE FUELS

	N_2H_4	MMH	UDMH
Boiling Point @ 1 Atm	113.5 C	87.5 C	63 C
Vapor Pressure @ 25 C	14.38 mm Hg	49.63 mm Hg	157 mm Hg
Latent Heat of Vaporization	9.600 kcal/mole @ 113.5 °C	9.648 kcal/mole @ 25 °C	8.37 kcal/mole @ 25 °C
Saturation Mole Fraction at 25 °C, 1 Atm	.0189	.0654	.206
Saturation Mass Fraction with N_2 at 25 °C, 1 Atm	.0216	.103	.358

in mixtures with nitrogen at one atmosphere, are also given. At higher pressures, saturation mole fractions and mass fractions will be smaller; at higher temperatures, they will be larger.

The presence of the noncondensable gas, such as nitrogen, will tend to lower the flame temperature considerably, particularly in the case of N_2H_4 . Formation of oxides of nitrogen will actually be reduced by extra nitrogen but there might be considerable difficulty obtaining complete combustion. One solution might be combustion at a very lean hydrazine-air ratio, with large amounts of natural gas or other auxiliary fuel used to provide an adequate flame temperature. In this case, however, destruction rates would be very low and there is still some question whether the percentage of hydrazine actually destroyed would be increased significantly, or whether the hydrazine discharge would simply be considerably diluted by the excess air and other combustion products.

An alternate solution might be the use of hydrogen, with its very high flame temperature and wide combustion limits, as the auxiliary fuel.

III. A. 3. Environmental Standards

Environmental standards are the same as those presented in Section II A, Incineration of Liquid Hydrazines.

III. A. 4. Overall Evaluation

We believe that the incineration of hydrazine vapors is potentially a thoroughly acceptable disposal method. Among other possibilities, both the SUE burner described in Section II A, Incineration of Liquid Hydrazines, and the Martin flare burner described in Section V. B, Nitrogen Tetroxide Vapors, could perhaps be modified to accommodate hydrazine vapors.

We do not believe that such modifications will necessarily be simple or straightforward, however, primarily because of the low saturation concentrations described in Subsection 2 above. In particular, it seems likely that a vapor burner might be developed which would look very satisfactory in operation, but which would actually be doing little more than burning an auxiliary fuel and diluting the hydrazine vapor to low concentration.

An acceptable burner for hydrazine vapor should be reasonably small, with short preheat times and reasonably low secondary fuel consumption, and should be capable of actually destroying dilute mixtures of hydrazine vapors in relatively inert carrier gases such as nitrogen. Until such a burner is developed and conclusively demonstrated, we must judge this disposal method unacceptable for current application.

B. VAPOR SCRUBBING

III. B. 1. Current Applications

At least three organizations contacted in Phase I of this study vent hydrazine vapors through water scrubbers. The water from the scrubbers is then discharged to either a neutralization or an oxidation pond. Other organizations vent directly to the atmosphere, usually with some sort of meteorological checks and restrictions.

III. B. 2. Chemical Description

The pertinent equations are:

1. $N_2H_4 + H_2O \longrightarrow$ Solution of N_2H_4 and NH_3 or amines
2. $CH_3 N_2H_3 + H_2O \longrightarrow$ Solution of MMH and NH_3 or amines
3. $(CH_3)_2 N_2H_2 + H_2O \longrightarrow$ Solution of UDMH and NH_3 or amines
4. $N_2H_4 + (CH_3)_2 N_2H_2 + H_2O \longrightarrow$ Solution of N_2H_4 , UDMH and NH_3 or amines

This aqueous solution should then be treated in either a neutralization pond or an oxidation pond, as discussed in Sections II. C. and II. D.

III. B. 3. Environmental Standards

Environmental standards for hydrazine vapor are detailed in Section II. A, Incineration of Liquid Hydrazines. Environmental standards for liquid discharges are detailed in Section II. C, Chemical Treatment of Liquid Hydrazines.

III. B. 4. Basis for Evaluation

Published data on the actual performance of hydrazine vapor scrubbers have not been available. Informal contacts have indicated that field measurements have never shown significant concentrations of hydrazine vapors being discharged from scrubbers.

It should be remembered that the water scrubber, as shown by the equations in Subsection 2, is not an ultimate disposal system but simply a device for exchanging the vapor disposal problem for a liquid disposal problem. Since Section II of the portion of the report describes several acceptable methods of liquid disposal, this exchange seems to be a well-founded one.

III. B. 5. Overall Evaluation

Vapor scrubbing is the only disposal method currently in use for hydrazine vapors other than direct discharge to the atmosphere. There is no doubt that it is environmentally better than atmospheric discharge.

On the basis of information available, our assessment of this disposal method is that it is environmentally acceptable, provided the hydrazine-bearing liquid effluent is treated according to the principles set forth in Section II.

Two additional methods of treating hydrazine vapors were studied during Phase 3 of this study: condensation, and catalytic decomposition. Results are reported in the section on Alternate Disposal Methods.

C. VENT TO ATMOSPHERE

Venting of hydrazine vapors into the atmosphere is common practice; precautions vary from zero to fairly elaborate modeling to determine whether meteorological conditions are such that turbulent mixing will reduce concentrations below certain threshold values. Most common is for wind direction and velocity to be monitored; near-zero wind or certain wind directions can shut down operations.

The provisional maximum exposure limit (see Section II.A.) of 0.01 ppm in the atmosphere, if applied anywhere near the vent stack, would preclude venting directly to the atmosphere at significant flow rates on all but the windiest days. Even more liberal standards would place severe restrictions on vent operations. Very tall vent stacks alleviate the problem of concentrations at ground level under most conditions, but there is no guarantee that air pollution standards will be applied only at ground level.

In view of all these considerations, it is our conclusion that direct atmospheric venting of hydrazine vapors is an environmentally unacceptable disposal method except in special cases where only minute vapor quantities are involved.

IV. DISPOSAL OF LIQUID NITROGEN TETROXIDE (DINITROGEN TETROXIDE - N_2O_4)

A. INCINERATION

IV. A. 1. Current Applications

Of the many incinerators now on the market, at least a few seem suitable for propellant disposal. One, designed by Thermal Research and Engineering Corp., of Conshohocken, Pennsylvania, has been in use at Cape Canaveral over a decade and still seems to be giving very satisfactory performance; it has been used for disposal of aqueous solutions of hydrazines and N_2O_4 . Thermal has not designed any other incinerators for this purpose since then, but is still active in burner design and emissions control. The Marquardt Company of Van Nuys, California, markets commercial fume incinerators and liquid incinerators which are an outgrowth of their work in the ramjet combustion field, and have run tests on disposal of N_2H_4 , UDMH, and N_2O_4 in their Sudden Expansion (SUE) incinerator.

IV. A. 2. Thermochemical Aspects

Table XVII lists some of the physical properties of nitrogen tetroxide. The liquid is an equilibrium mixture of NO_2 and N_2O_4 , brown in color, that is prepared industrially from nitric oxide (NO) and air. At 20 °C, the equilibrium composition of the liquid is 16% NO_2 , 84% N_2O_4 . N_2O_4 vapors are colorless, but they decompose very rapidly to form NO_2 ; at equilibrium at 25 °C, one atmosphere, the N_2O_4 is 27% dissociated.

NO_2 is one of the most insidious gases known. Inflammation of lungs may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal.

Threshold Limit Value (TLV) as recommended by the American Conference of Government and Industrial Hygienists (ACGIH) is 5 parts per

million in air, or 9 milligrams per cubic meter of air.

N_2O_4 does not burn, but supports the combustion of carbon, phosphorous, and sulfur. It is soluble in concentrated sulfuric and nitric acids, decomposes in water forming nitric acid (HNO_3) and nitric oxide (NO), and reacts with alkalies to form nitrates and nitrites. It is corrosive to steel when wet, but may be stored in steel cylinders when moisture content is 0.1% or less.

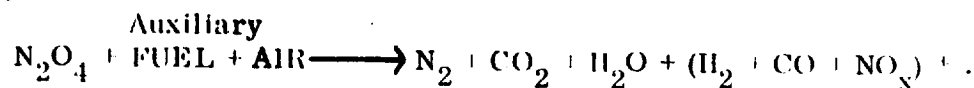
TABLE XVII
PHYSICAL PROPERTIES OF N_2O_4

Molecular Weight	92.02
Color	Colorless (NO_2 is red brown gas)
Nitrogen	30.45%
Oxygen	69.55%
Density $\frac{20}{4}$	1.448 g/CC
Melting Point	-9.3 C
Boiling Point	21.3 C
Heat of Vaporization at 21.0°C	99.0 cal/g = 4555 cal/mole (NO_2)
Critical Temperature	158.2 C
Critical Pressure	100.0 atm

NO_2 and N_2O_4 are dangerous. When heated they evolve highly toxic fumes; they will react with water or steam to produce heat and corrosive liquids; they can react with reducing materials. The odor thresholds for NO_2 are less than 0.5 ppm.

N_2O_4 decomposes relatively easily and supports combustion. With proper feed rates and the use of auxiliary fuels combustibility is readily controllable. Temperature can be controlled over some range by varying the air/fuel ratio. A minimum temperature must be maintained for satisfactory decomposition of wastes; rates of reaction are increased rapidly by higher

temperatures. Combustion at high temperatures, however, slowly converts atmospheric N_2 to NO. This NO is oxidized, either slowly by O_2 or rapidly by O_3 , to produce NO_2 . Combustion can be described by the following equation:



* traces

The degree of turbulence in the reaction zone significantly affects the incinerator performance. Intimate mixing of the fuel and NO_2 is required for completeness of combustion. Ideally, adequate destruction of waste propellant is the reduction of N_2O_4 to N_2 with minimum NO formation. Effectiveness is judged by the combustion results as indicated by stack effluent analysis.

Thermal Research and Engineering Corp. has discussed a number of methods used to control NO_x emissions during combustion processes. An equilibrium burner with good internal recirculation characteristics produces low NO_x levels because the mixing at equilibrium leaves little oxygen for nitrogen oxidation. Another technique uses two stage combustion where the fuel is burned with less than theoretical air in the primary stage. Air is injected into the second stage to burn the remainder of fuel. A third procedure is flue gas recirculation. The gas at the end of combustion is recirculated into the combustion chamber. The result is lower flame temperatures and oxygen concentrations because of dilution with relatively inert gas. This treatment is not generally used for low NO_x concentrations. For low concentrations magnesium hydroxide scrubbing is promising. Also sulfuric acid scrubbing or ammonia reduction and scrubbing are possibilities.

The theoretical compositions of the products of combustion of various combinations of N_2O_4 , natural gas, propane and air were computed by the Marquardt Company as part of Air Force Rocket Propulsion Laboratory Contract No. FO 4611-73-C-0007.¹ These computations were based on NASA Report SP-273, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations" by Sanford Gordon and Bonnie J. McBride,

¹ Joel E. Hutson, "Toxic Waste Burner Evaluation", Final Report, AF-RPL Contract No. F04611-73-C-0007 (Marquardt Report S-1271), November 1973.

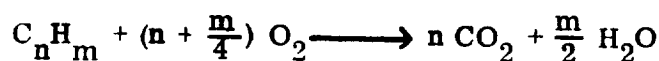
1971. The results are reproduced in Figures 10 through 12 as useful guidelines for future equipment evaluation. Figure 11 indicates that satisfactory operation can be obtained at over-stoichiometric conditions with little excess air present. Thus, a weight ratio of propane to N_2O_4 which is somewhat less than 0.45 results in less than 200 parts per million of NO production.

Figure 11 also shows that hydrogen is produced from traces up to 4×10^5 ppm. When the stoichiometric ratio of propane to N_2O_4 is used 4×10^4 ppm of hydrogen is produced. Carbon monoxide (CO) is produced from traces up to 3.5×10^5 ppm. At the stoichiometric ratio of propane to N_2O_4 about 1.4×10^5 ppm are produced. Nitric oxide and nitrogen dioxide are formed from traces up to over 2×10^4 ppm. At the stoichiometric ratio of propane to N_2O_4 about 1.5×10^4 ppm are produced.

Operation of an incinerator at lean fuel/ N_2O_4 ratios with high air/fuel ratios is not feasible due to the low temperature and consequent abundant NO_x gas release into the atmosphere. For this reason, under-stoichiometric burning with N_2O_4 and air is not considered practical. (The results shown in Figure 12 seem to be primarily dilution effects rather than thermochemical effects.)

Operation at over-stoichiometric incineration (fuel/ $N_2O_4 > 0.4$) and with relatively high fuel/air ratio and higher temperature is more desirable. Under these conditions more fuel is used and more CO and H_2 generated but the amount of NO_x formed is considerably reduced.

Additional discussion of incinerators, and formation of oxides of nitrogen is presented in Section II A, Incineration of Liquid Hydrazines. One aspect of combustion not discussed in that section might be especially significant in the case of destruction of an oxidizer, however; the possibility of formation of reactive hydrocarbons. For the complete destruction of an oxidizer, it is necessary for an incinerator to operate at fuel-rich conditions, which favor the formation of intermediate products that can be released to the atmosphere. The complete combustion of a hydrocarbon results in the formation of carbon dioxide and water,



but the reaction of the same hydrocarbon with insufficient oxygen results in

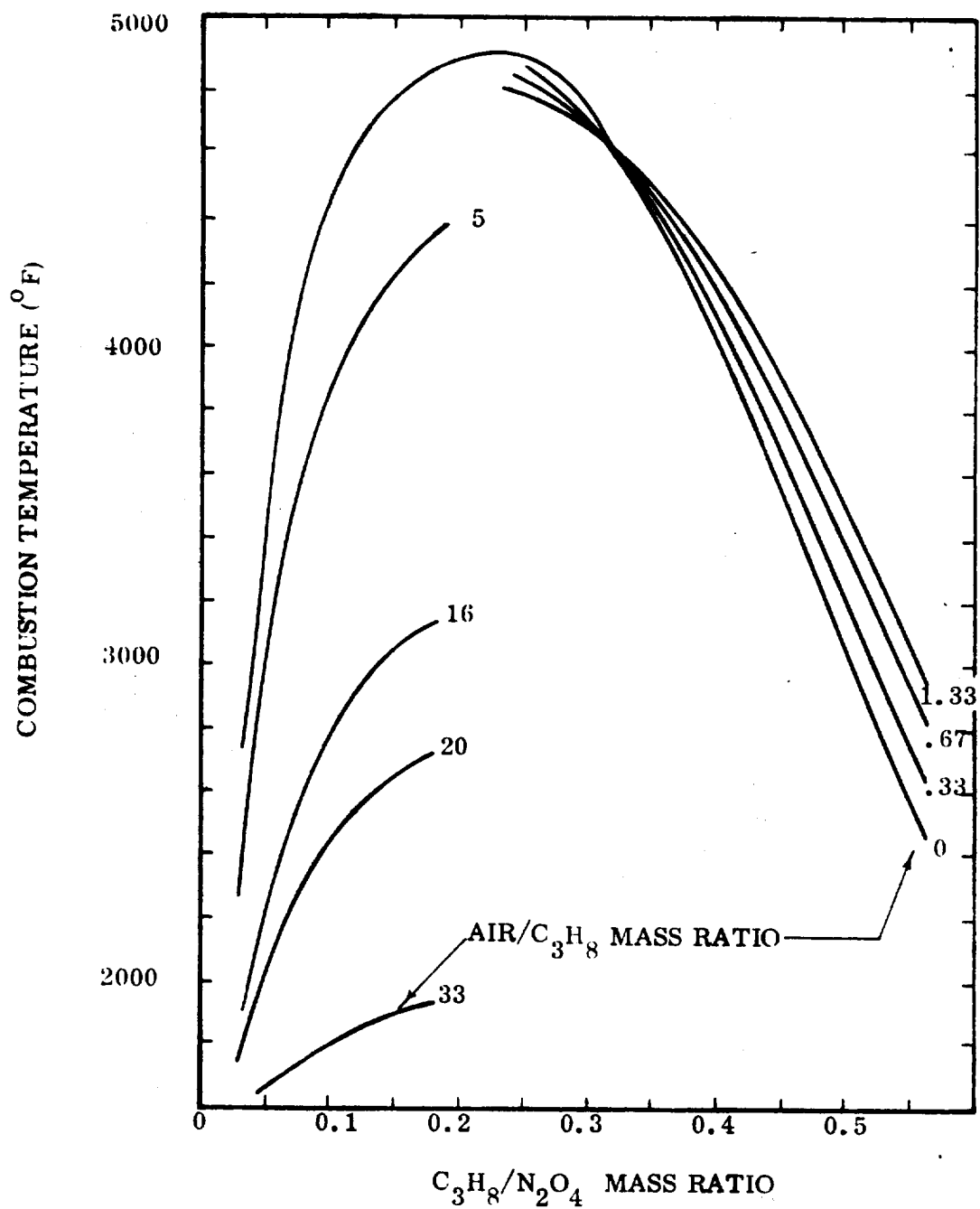


FIGURE 10
 ADIABATIC FLAME TEMPERATURES FOR
 N_2O_4/C_3H_8 / AIR COMBUSTION
 (from Marquardt Co. Report S-1271)

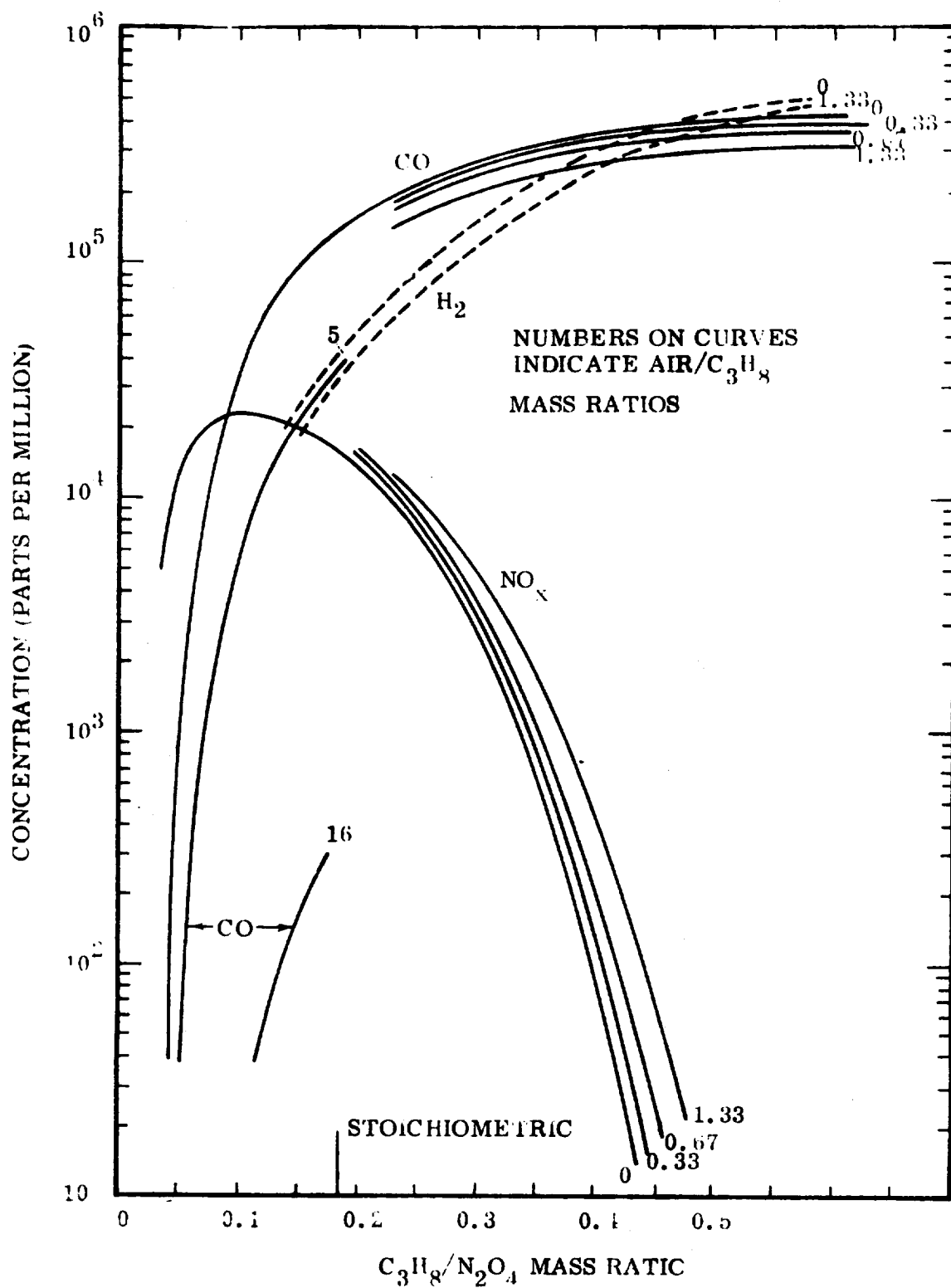


FIGURE 11
THEORETICAL EQUILIBRIUM PRODUCTS FOR
 N_2O_4/C_3H_8 /AIR COMBUSTION
(from Marquardt Co. Report S-1271)

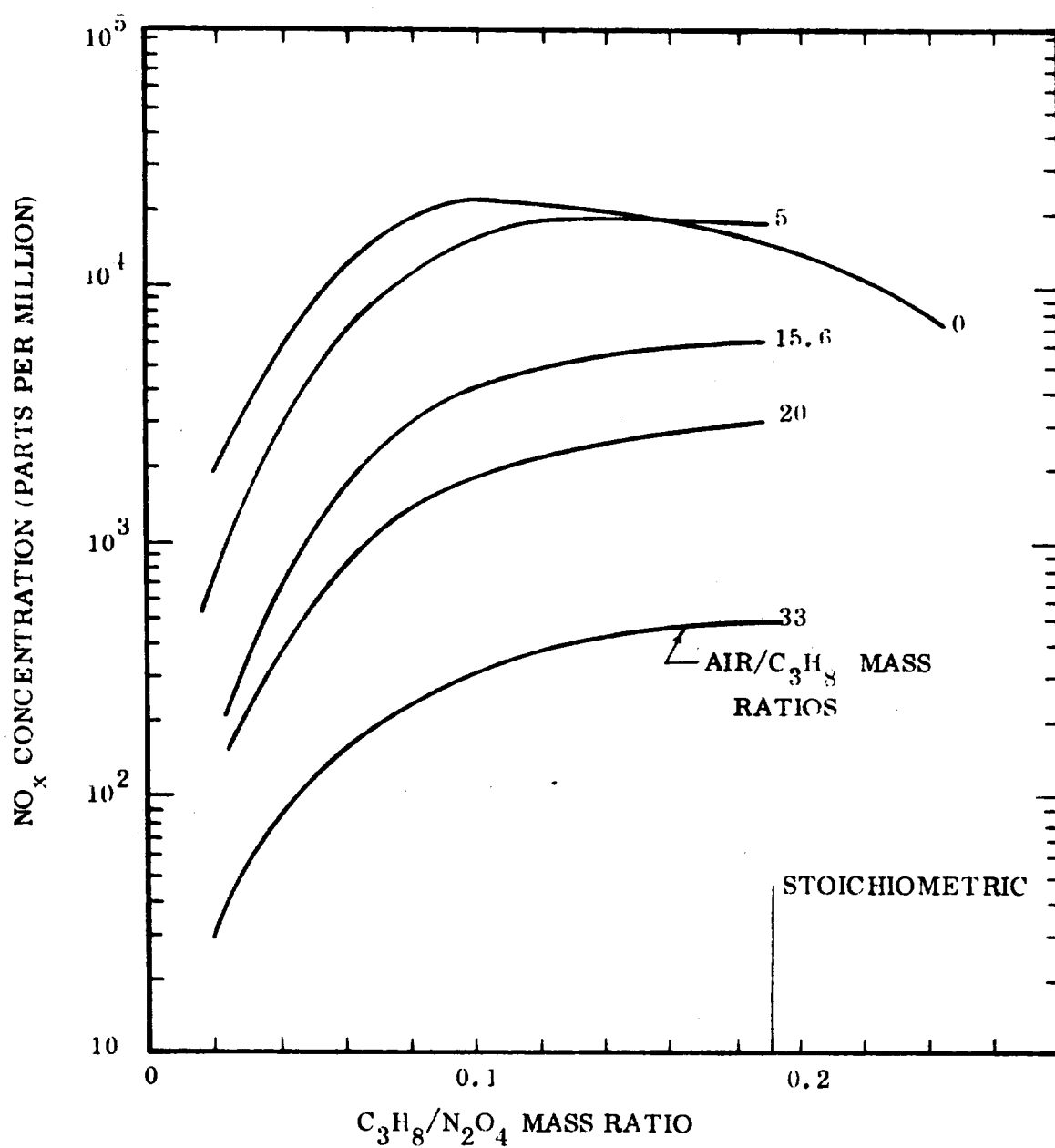


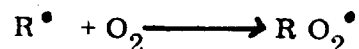
FIGURE 12

EQUILIBRIUM NO_x CONCENTRATIONS FOR
 UNDER-STOICHIOMETRIC $\text{N}_2\text{O}_4/\text{C}_3\text{H}_8/\text{AIR}$ COMBUSTION
 (from Marquardt Co. Report S-1271)

the formation of an aldehyde and an alkyl radical,



The aldehyde, RCHO, is a smog-former, and the alkyl radical can react with another oxygen molecule to form a peroxyalkyl radical,



which in turn tends to oxidize nitric oxide to nitrogen dioxide,



Although the entire complex sequence of chemical and photochemical reactions that give rise to smog is still largely unknown, these reactions are thought to be some of the most important.² Their severity is somewhat diminished in our case by the fact that the reactivity of exhaust emissions is known to be very low in cases where propane or methane is the parent fuel.

IV. A. 3. Environmental Standards

The State of Florida has the following environmental standards for nitrogen dioxide:

Alert Status	0.6 ppm	over period of	one hour
Warning Status	1.2 ppm	over period of	one hour
Emergency Status	1.6 ppm	over period of	one hour
Alert Status	0.15 ppm	averaged over	24 hours
Warning Status	0.30 ppm	averaged over	24 hours
Emergency Status	0.40 ppm	averaged over	24 hours

Continued exposure of plant life to NO₂ will change the flora of the environment. The following chart denotes susceptible and resistant species:

² Edward F. Obert, Internal Combustion Engines and Air Pollution, Intext Educational Publishers, New York, 1973, pages 363-373.

SENSITIVITY OF SELECTED PLANTS TO NITROGEN DIOXIDE

Sensitive

Azalea - *Rhododendron* species
Bean, pinto - *Phaseolus vulgaris* L.
Brittlewood - *Melaleuca Leucadendra*
Hibiscus - *Hibiscus rosasinensis*
Lettuce (head) - *Lactuca sativa* L.
Mustard - *Brassica* species
Sunflower - *Helianthus annuus* L.
Tobacco - *Nicotiana glutinosa* L.

Intermediate

Cheeseweed - *Malva parviflora* L.
Chickweed - *Stellaria media* Cyrill
Dandelion - *Taraxacum officinale* Weber
Grass, annual blue - *Poa annua* L.
Orange - *Citrus sinensis* Osbeck
Rye - *Secale cereale* L.

Resistant

Asparagus - *Asparagus officinalis* L.
Bean, bush - *Phaseolus vulgaris* L.
Carissa - *Carissa carandas*
Grass, Kentucky blue - *Poa pratensis* L.
Heath - *Erica* species
Ixora - *Ixora* species
Lamb's-quarters - *Chenopodium album* L.
Nettle-leaf goosefoot - *Chenopodium* species
Pigweed - *Chenopodium* species

Source: Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas,
J.S. Jacobson and A.C. Hill, Eds., Air Pollution Control Association
and National Air Pollution Control Association, Pittsburgh, Pa. 1970.

The State of Florida also has the following environmental standards for carbon monoxide:

Alert stage	15 ppm	8 hours average
Warning stage	30 ppm	8 hours average
Emergency stage	40 ppm	8 hours average

At the present time there are no standards for hydrocarbons.

Established toxicity levels for NO and NO₂ are given in Table XI, Section IIA, Incineration of Liquid Hydrazines. Established criteria for planned and accidental releases are given in Table XII of the same section. The TRW report³ does not specifically treat oxides of nitrogen, but our assumption is that the usual standard for provisional Maximum Exposure Limits - one per cent of the TLV's - would also apply here, yielding 0.25 ppm for NO, 0.05 ppm for NO₂.

IV. A. 4. Bases for Evaluation

Table XVIII, compiled from available analytic reports,^{4,5,6,7} shows the high and low concentration of combustion products from incineration of N₂O₄. A study of these reports shows that under optimum conditions only small quantities (5 - 500 ppm) of NO_x pollutant are formed, but up to 10 or 20 times these amounts can form under non-optimum conditions.

It should be noted that all of these data were obtained from two incinerators - the Thermal Research incinerator installed at ETR, and the Marquardt SUE incinerator. These incinerators are quite different in concept.

³Op. cit., Vol XII.

⁴Pan Am Internal Report U 327, dated 3 January 1972.

⁵Pan Am MD-EH Internal Report, dated 26 February 1971.

⁶Pan Am Internal Report dated 8 October 1970.

⁷Joel E. Hutson, op. cit.

TABLE XVIII
CONCENTRATION OF N_2O_4 COMBUSTION PRODUCTS

	Low	High
NO_x , ppm *	250	7990
CO, ppm or %	1 ppm	.5%
CO_2 , %	8.3	16.7
O_2 , %	4.6	7.9
H_2 , ppm or %	no data	no data
Total HC, ppm	4	40.1
HC (As CH_4), ppm	23	17,010

* Thermal Research Incinerator, ETR

the Thermal Research unit being a very large incinerator that handles N_2O_4 as a dilute aqueous solution, and the SUE incinerator being the relatively small, quick-response unit described in Section II. A. , Incineration of Liquid Hydrazines. Both the highest and lowest figures for NO_x were recorded with the Thermal Research unit; all of the test runs with the SUE unit produced off-scale (> 2000 ppm) NO readings.

The Thermal Research unit is not currently being used to destroy waste nitrogen tetroxide, and possesses the disadvantages of other large incinerators in terms of auxiliary fuel consumption and long preheat cycles. The SUE results, however, require further discussion.

The SUE Test program, using N_2O_4 , was prematurely terminated after only a few runs, and the Marquardt report⁸ describes the results as "inconclusive". Satisfactory N_2O_4 destruction, in terms of no noticeable exhaust color or odor, was obtained in two ways:

⁸ Op. cit. , page 31.

1. "by... achieving rich combustion with C_3H_8 and air only; then simultaneously bringing in N_2O_4 , increasing C_3H_8 , and decreasing air until sufficient fuel was available to theoretically provide over-

stoichiometric burning of both air and N_2O_4 ."⁹

2. "at a constant $C_3H_8 : N_2O_4$ ratio and decreasing amounts of air As air flow was reduced ... the exhaust cleaned up until no discoloration or odor was noticed."⁹

In neither case, however, was it possible to bring NO emissions within the range of the instrumentation.

By way of explanation of the high NO readings, the author points out that "There are several possibilities such as instrument error in NO measurements or flow rate errors in propellant meters."¹⁰ There are also other possibilities more closely related to the actual incinerator performance.

A comment is probably in order at this point regarding discrepancies between theoretical and observed products of combustion. There is no reason to expect that the equilibrium compositions of Figures 10 through 12 (or 2 through 5) will necessarily be achieved in any particular incinerator. In particular, failure to achieve the desired results can be caused by the following:

1. Failure to achieve equilibrium, through poor mixing, short stay times, etc. The theoretical calculations are made on the basis of all reactions going to completion.
2. Non-uniform incinerator flow conditions. Measured inlet flow rates give average values only for mixture ratios; local variations could result in different product compositions at different points in the incinerator. In particular, local hot spots can result in large NO formation in almost any sort of air-breathing combustion chamber.

⁹Op. cit., page 32.

¹⁰Op. cit., page 33.

We are not at this point presenting any conclusions regarding the SUE burner's performance in this respect, but merely recording some of the possibilities. Recommendations for further work made in the Marquardt report include "re-evaluation of the incineration configuration and injection system". ¹¹

In the various reports used to compile Table XVIII, a variety of techniques were used to measure NO and NO₂ concentrations, mostly based on commercially available instrumentation. One method in particular that should be recorded at this point is an analytical method developed by the Pan American Environmental Health Laboratory to enable determination of NO₂ in air down to 0.01 ppm. A general description is quoted.

Nitrogen dioxide is determined by the diazotization of sulfanilic acid and subsequent coupling with N- (1-naphthyl) - ethylenediamine to form a deep red color.

Apparatus:

1. Spectrophotometer for use at 540 mu. One cm. light path cells are used for moderate concentrations.
2. 50 ml. volumetric flasks
3. 25 ml. pipettes

Reagents:

1. Sulfanilic Acid Absorbing Reagent: Dissolve 5 g. of sulfanilic acid in approximately 500 ml. of demineralized water in a 1000 ml. volumetric flask. Add 140 ml. of glacial acetic acid and 20 ml. of 0.1% N - (1-naphthyl) - ethylenediamine. Dilute to 1000 ml. with demineralized water. Store in brown bottle in the refrigerator.
2. Sodium Nitrite Stock Solution (for water samples): Dissolve 0.1568 g. of anhydrous sodium nitrite in 500 ml. of demineralized water in a volumetric flask. Add 1 ml. of chloroform (CHCl₃) as a preservative and make up to 1000 ml. with demineralized water. One ml. produces the color equivalent of 100 mg. of nitrogen dioxide.
3. Sodium Nitrite Stock Solution (for air samples): Dissolve 0.0203 g. of anhydrous sodium nitrite in 500 ml. of demineralized water in a volumetric flask. Add one ml. of chloroform (CHCl₃) as a preservative, and make up to 1000 ml. with demineralized water. One ml. of this solution produces the color equivalent of 10 ml. of nitrogen dioxide. (10 ppm in one liter of air at 760 mm. of Hg at 25 C).

¹¹ Ibid.

Procedure:

1. Pipet 25 ml. (or a known volume) of sample into a 50 ml. volumetric flask.
2. Fill the flask with absorbing reagent.
3. Let stand for 15 minutes.
4. Measure optical density at 550 mu. Use 5 cm. cells if color is faint.

Sample Preparation:

Air samples can be drawn through 10 ml. of absorbing reagent in a bubbler or into an evacuated flask containing 10 ml. of absorbing reagent. In the latter case, at least 15 mins. (with occasional shaking) should be allowed for complete color development. Interference in color production by other nitrogen oxides is negligible. Sulfur dioxide in relatively high concentrations (100-1000 ml.) and chlorine reduce the color formed.

IV.A.5. Overall Evaluation

The theoretical results in Subsection 2 above indicate that a well-designed incinerator, operating with carefully-chosen N_2O_4 / fuel air ratios, should be capable of successfully destroying N_2O_4 with relatively little formation of NO or other dangerous emissions. The data in Subsection 4, however, show that these results have not yet been demonstrated in a small, quick-response incinerator. Environmentally acceptable destruction has been obtained in the large Thermal Research incinerator, although apparently not with great consistency. As we commented in discussing incinerators for liquid hydrazines, the overall environmental impact of a large burner with high fuel consumption and long pre-heat periods might be much more adverse than considerations of trace species concentrations in the effluent would indicate.

The SUE incinerator has waste destruction rates comparable to the large traditional units - up to 0.313 pounds per second in the Marquardt tests, or about 1.5 gallons per minute (8000 gallons in 90 hours). If low NO emissions could be demonstrated, this unit would be extremely attractive. As discussed in the evaluation of incinerators for liquid hydrazines, other small incinerators could also be developed for this purpose, and a higher degree of application of advanced combustor technology could probably be expected.

There is an inherent problem regarding destruction of oxidizers rather than fuels through combustion that cannot be overlooked. Complete destruction in this case requires rich, rather than lean, mixture ratios. Fuel-rich combustion is almost always less environmentally acceptable than lean combustion because of the formation of partial products such as CO, ketones, aldehydes, olefins, etc.

Our overall evaluation is that incineration of N_2O_4 waste is theoretically an acceptable means of destruction. In practice, it has not been adequately demonstrated to date from the standpoint of NO emissions, although in other respects it appears to be successful.

B. CHEMICAL NEUTRALIZATION

IV. B. 1. Current Applications

By far the most common means of disposing of N_2O_4 is dilution followed by neutralization. The chemical industry recommends soda ash, lime, or other alkali for neutralization. Substances used by the organizations contacted include sodium carbonate, triethanolamine, and sodium hydroxide. Several have diluted and added the mixture to the same holding ponds used for hydrazines; these ponds were then neutralized using sodium hydroxide or hydrogen peroxide with copper sulfate catalyst, or both. Additional details on all these approaches are given in the portion of this report on Phase 1, Current Disposal Methods.

IV. B. 2. Chemical Description

The process for treating waste N_2O_4 is similar to that used for treating N_2H_4 except that all the reagents are basic. Chemical neutralizations initially require dissolution of N_2O_4 , which is converted to nitric acid (HNO_3) and nitrous acid (HNO_2). These acids are subsequently neutralized with suitable alkali, as shown in the following equations and in Table XIX.

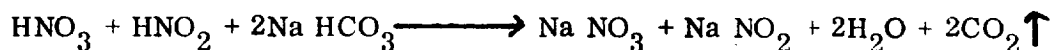
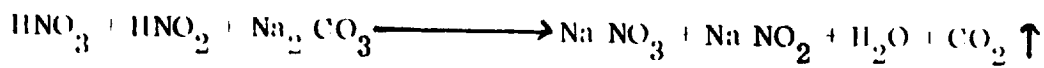


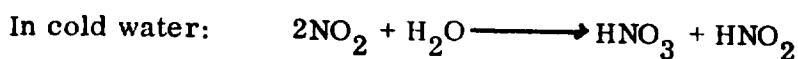
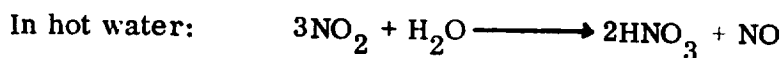
TABLE XIX

NEUTRALIZATION OF N_2O_4

Method	Neutralizing Reagent	Products Formed	Safety of Reagent	Cost of chemical lb N_2O_4	Pollution
1	Na H CO_3	Solutions of NaNO_3 and NaNO_2 , H_2O CO_2	Innocuous	\$.165	Na^+ , NO_3^- , NO_2^- Effluent may be sive due to NO_3 and NO_2 ions toxic and corro-
2	Na_2CO_3	Solutions of Na salts, H_2O , CO_2	Innocuous	\$.15	Same as above
3	Ca (OH)_2	Solutions of Ca salts, H_2O	Skin irritant - Inhalation hazard	\$.08	Ca^{++} , NO_3^- , NO_2^- Effluent may be sive due to NO_3 and NO_2 ions toxic and corro-
4	Na OH	Solutions of Na salts	Corrosive to all tissues	\$.025	Na^+ , NO_3^- , NO_2^- Effluent may be toxic and corrosive
5	Mg (OH)_2	Solutions of Mg salts	Innocuous	\$.57	NC_3^- , NO_2^- , Mg^{++} Effluents may be toxic and corrosive



NO_2 reactions differ in hot and cold water.



Triethanolamine was not included in Table 10 because of a reported explosion resulting on one occasion by neutralizing insufficiently diluted N_2O_4 , as well as its relatively high cost.

The products of N_2O_4 neutralization are NO_3^- , NO_2^- , with the metallic ion of the reagent and CO_2 if a carbonate is used. The precautions for handling hazardous materials apply as well to N_2O_4 as to N_2H_4 .

The effluents are inconspicuous and contain ions of NO_3^- , NO_2^- , Na^+ , Ca^{++} , or Mg^{++} , depending on which neutralizing reagent is utilized. The effluent may be toxic and corrosive due to NO_3^- and NO_2^- ions present up to a few tenths of 1%.

The urea reaction given in the literature is not utilized by any company contacted.

IV. B. 3. Environmental Standards

The State of Florida has ruled that drinking water shall contain no more than 45 ppm of nitrates and that sewage effluent contain no more than 3.0 ppm of nitrates analyzed as nitrogen. Other pertinent standards are:

1. a limit of 80-100 ppm of CaCO_3 in city drinking water.
2. a limit of 500 ppm in total dissolved solids in city drinking water.

Most cities will treat water until the above standards are met. New regulations pertaining to each specific industry are currently being written, however. Table XV, in Section II. C., Chemical Treatment of Liquid Hydrazines, lists recommended provisional limits for a number of other possible neutralization pond effluent constituents.

IV. B. 4. Bases for Evaluation

The most important consideration in evaluating the neutralizing agents is the effectiveness of the agent and its safety properties. All the neutralizing agents are essentially equally effective but the strong bases $\text{Ca}(\text{OH})_2$ and NaOH are a hazard in that they can cause severe burns if accidental skin contact occurs. The second most important consideration is the environmental hazard. Calcium and magnesium salts can harden water and thus present an environmental disposal problem. The combined weight of NO_3^- and NO_2^- ions will be approximately the same for all reagents and present equivalent problems. The least important consideration is cost. The cost of neutralizing one pound of N_2O_4 with each neutralizing reagent is listed in Table XIX.

IV. B. 5. Overall Evaluation

Each neutralizing agent is given a rating 1 through 3 in each of the following three categories. Each of these categories is also rated according to its importance as shown in parentheses, i.e., a weighting factor yielding a possible maximum total of 18 points.

- (3) Safety and Effectiveness
- (2) Environmental Hazard
- (1) Cost

The ratings are shown in Table XX. The rating of each compound is multiplied by the rating of each category. These three products are summed to yield a number indicative of the overall advantages of each neutralizing agent. For example, a rating of 3 in Safety and Effectiveness means the

TABLE XX
RATINGS OF N_2O_4 NEUTRALIZING AGENTS

Neutralizing Agent	Safety & Effectiveness (3)	Environmental Hazard (2)	Cost (1)	Total Points
Na H CO_3	3	3	2	17
$\text{Na}_2 \text{ CO}_3$	3	3	2	17
Ca (OH)_2	1	1	3	8
Na OH	1	3	3	12
Mg (OH)_2	2	1	1	9
Urea	1	3	2	11
Triethanolamine	1	3	1	10

agent is essentially harmless and yields a harmless product upon reaction with N_2O_4 . A rating of 2 or 1 means the agent has important disadvantages in this category. A rating of 3 in the environmental hazard category means the product of reaction with N_2O_4 is as harmless to the environment as can be expected. A rating of 2 or 1 means that the product constitutes a more serious environmental hazard. A rating of 3 in cost means the price ranges from \$0.01 to \$0.10 to neutralize one pound of N_2O_4 . A rating of 2 indicates the cost range of \$0.11 to \$0.20. A rating of 3 is anything beyond \$0.21.

Thus it is seen from the table that the agents $NaHCO_3$ and Na_2CO_3 seem to be overall the most advantageous neutralizing agents for N_2O_4 .

In terms of evaluating chemical means of destroying N_2O_4 , a brief quantitative example is probably in order. It is estimated that approximately 480 gallons of N_2O_4 will be vaporized during the loading of 8000 gallons onto the Space Shuttle. If it were necessary to dispose of such an amount of liquid N_2O_4 , by neutralization with $NaHCO_3$, 5.28 tons of the neutralizing agent would be required at a cost of roughly \$1000. The cost figure seems reasonable but the bulk of $NaHCO_3$ that would have to be handled and used makes neutralization feasible but unattractive. Also, this neutralization would produce approximately 4403 Kg (9686 lbs.) of sodium nitrate and sodium nitrite. In order to maintain the same environmental standards as a sewage plant this material would have to be diluted with approximately 3.9×10^{11} gallons of water. This is clearly impractical. An alternative would be to allow the neutralized solutions to sit in holding ponds and allow evaporation to occur. The solid nitrate and nitrite could then be trucked away and used as fertilizer.

C. SIMPLE DILUTION WITH WATER

IV.C.1. Current Applications

None of the organizations contacted during Phase 1 of this study reported that simple dilution and discharge of liquid N_2O_4 is being practiced, although it seems likely that at least for small quantities this method sees widespread, if informal usage. Three organizations reported dilution fol-

lowed by discharge to general purpose holding ponds, with no further formal treatment; reaction with dilute hydrazine fuels in the same holding ponds is probably significant in many cases, however.

IV.C.2. Chemical Description

With cold H_2O , N_2O_4 forms nitric and nitrous acids according to the equation.



IV.C.3. Environmental Standards

The State of Florida requires that when dumping an acid into a stream the pH of the stream must not be changed more than 1.0 pH unit. 0.1 N nitric acid has a pH of 1.2. Thus dilution to 1×10^{-6} N would be required to produce a pH of 6.0. This dilution would require 1.6×10^6 gallons of water per gallon of N_2O_4 . Alternatively, dilution of N_2O_4 to a pH of 1.0 would require approximately 160 gallons of water per gallon of N_2O_4 , and would leave an effluent of such low pH as to be still clearly hazardous.

IV.C.4. Overall Evaluation

This method is environmentally acceptable if sufficient water is available to allow dilution to a pH of 6 prior to discharge. The practicality clearly depends on the amount to be diluted and the availability of water. For disposal in significant quantities, attention would have to be given to means of assuring proper dilution. For example, a holding pond where pH could be monitored prior to release would be acceptable, as would a steady flow mixing apparatus; more casual dilution methods would not be acceptable.

This method has an advantage over chemical neutralization and incineration in that nothing "extra" is added to the disposal problem. Both other methods result in the need to dispose of calcium or sodium salts, or possibly to discharge hydrocarbons to the atmosphere. On the other hand, the other methods result in more positive elimination of the N_2O_4 .

D. DISPOSAL AS A VAPOR

The disposal methods outlined above all treat the nitrogen tetroxide as a liquid. Since the boiling point of nitrogen tetroxide is 21°C at one atmosphere pressure, it is also feasible to evaporate the liquid and dispose of the vapor according to one of the methods described in the following sections. Two of these methods - the absorption (scrubbing) techniques - simply amount to returning the vapor to a liquid state. The other two - flare burners and atmospheric venting - are essentially different disposal techniques from those discussed in the preceding sections, and might represent additional viable methods for disposal of liquid nitrogen tetroxide.

V. DISPOSAL OF NITROGEN TETROXIDE VAPORS

A. FLARE BURNERS

V.A.1. Current Applications

A proprietary Martin-Marietta Corp. flare burner, designed and developed during the late 1960's, has been installed at the Johnson Space Center, Houston, Texas; Western Test Range, Vandenberg Air Force Base, California; and White Sands Test Facility, Las Cruces, New Mexico; as well as at Martin-Marietta's Denver Division. The unit was originally designed for use at Titan II sites, and it seems likely that a number are also currently located at these installations. This design is the only one we know of that has been used for disposal of nitrogen tetroxide vapors.

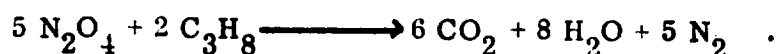
This unit consists basically of a cylinder (one standard configuration is 8" diameter by 3' long) containing a plenum in which propane and waste N_2O_4 vapors are injected, and a burner head. The plenum is designed in such a way that the propane and oxidizer don't come into contact with each other until they reach the exit plane of the burner. A wind shroud protects the head from flame out. A continuous pilot is provided at the top of the burner head to ignite the gas mixture. Approximately 10 pounds per minute of N_2O_4 can be destroyed in the case of the 8 inch configuration. Essentially, the brown NO_2 vapors from N_2O_4 are reduced to N_2 and a small amount of NO , which are colorless (and therefore invisible) gases.

A larger version of this burner, with a capacity of 30 pounds per minute of N_2O_4 , was recently installed at Johnson Space Center.

V.A.2. Thermochemical Aspects

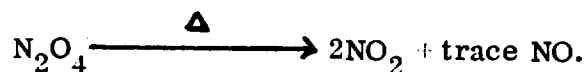
The unit is basically similar in its principles of operation to the incinerators discussed in Section IV. A. , Incineration of Liquid Nitrogen Tetroxide. Fundamental differences are that the combustion zone is external, rather than internal; there is no control over the air supply; and there is less latitude for refinement of the design (combustion chamber parameters, nozzles, secondary air, etc.). Testing is complicated by the fact that combustion is accompanied by uncontrolled dilution, and that the effluent is unconfined (giving rise to problems regarding where samples should be taken). On the other hand, the characteristic of a central C_3H_8 N_2O_4 flame, with an unlimited quantity of air available surrounding the flame, might well constitute a favorable environment for N_2O_4 destruction that would be difficult to duplicate in an internal combustion incinerator.

The stoichiometric equation for reaction of N_2O_4 with C_3H_8 is

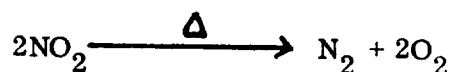
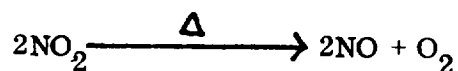


The limitations of this sort of equation have been discussed extensively in earlier sections on incineration, including the need for fuel-rich operation to assure complete destruction of N_2O_4 . In addition to reaction, however, dissociation is of prime importance in discussing N_2O_4 destruction.

At low temperatures (up to $200^\circ C$ or higher) N_2O_4 dissociates to form NO_2 , with only traces of NO :



At high temperatures ($2000^\circ C$ or higher) the NO_2 in turn dissociates according to two dissociation equations:



where if other constituents are predominantly oxidizing, the first equation is most important, but if they are strongly reducing the second dissociation predominates. In other words, fuel rich combustion also favors the desirable NO_2 dissociation, as opposed to the formation of NO . (These dissociation

considerations were implicit in the theoretical predictions reported in earlier sections on incineration.)

V.A.3. Environmental Standards

Environmental standards are detailed in Section IV.A., Incineration of Liquid N_2O_4 .

V.A.4. Bases for Evaluation

The only published data on effluents from these flare burners resulted from a test program conducted at White Sands Test Facility several years ago.¹ "Samples were obtained simply by holding an inverted funnel connected... to an evacuated 3-liter pressure bottle over the most dense portion of the flame," and were analyzed in an infrared spectrophotometer having detection limits of 1.0 ppm NO, 0.04 ppm NO_2 , 1.0 ppm CO, 0.1 ppm CO_2 , 0.1 ppm HC, 100 ppm H_2O . Results reported were simply that in a lean operating mode, NO and NO_2 were detected, whereas in the proper fuel-rich mode only H_2O , CO_2 and HC were detected. No carbon monoxide was detected in any of the samples. An interesting statement was that "No attempt was made to obtain samples that could be quantitatively analyzed to determine the exact output of the unit. Since wind conditions at the White Sands Test Facility are very erratic, sampling for precise quantitative analysis would be difficult and impractical."

We believe that these results illustrate our earlier statements regarding the difficulty of collecting meaningful data from this sort of external combustion device. The absence of both CO and NO from the same sample seems somewhat unlikely, except as a result of very considerable dilution. Perhaps, however, these results can be taken as evidence that the flare burner does not have any particularly severe NO problems in the fuel rich mode.

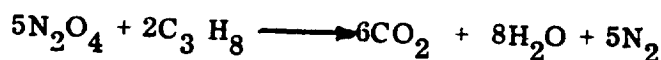
We have had some personal experience with the flare burner, in the form of a first hand demonstration. Certainly the unit is capable of destroying nitrogen tetroxide vapors without producing a visible plume. In a very fuel rich mode, it tends to be smoky. Whether its overall

¹Irwin D. Smith, Nitrogen Tetroxide Disposal Unit Combustion Products, NASA TN D-3965, May 1967.

performance is substantially different from that of the SUE burner described in Section IV. A. is impossible to determine, and would require a fairly extensive test program.

The scope of the Space Shuttle vapor disposal requirements can be estimated if we assume that 8000 gallons of N_2O_4 are handled during each loading, at a rate of 50 gallons per minute, with approximately 3 gallons per minute being lost through the vent system. For this example, total loading time is 160 minutes, and approximately 480 gallons of N_2O_4 passes through the vent system. The smaller flare burner can effectively dispose of N_2O_4 at the rate of ten pounds per minute. It would therefore take approximately 9.7 hours to destroy the 480 gallons of N_2O_4 vented during loading operations. Alternately, four small burners or two large burners would be required for instantaneous disposal with no requirement for vent gas storage.

If the N_2O_4 were destroyed in a stoichiometric ratio with propane as in the equation



then 2 moles of propane would be needed to destroy 5 moles of N_2O_4 , or 1 gram of propane for every 5.4 grams of N_2O_4 , or 1600 lbs. of propane to destroy 480 gallons of N_2O_4 . This cost would be about \$98 calculated at a propane price of \$0.30 per gallon. Actually, because of the need for fuel-rich operation, the fuel cost would be somewhat higher, but certainly not enough to become a particularly significant cost factor.

V. A. 5. Overall Evaluation

The flare burner is considered to be an environmentally acceptable means of disposing of nitrogen tetroxide vapors, or of liquid nitrogen tetroxide if a suitable evaporation chamber is incorporated. It is not as infallible as some systems, because it is affected by atmospheric conditions such as strong winds, and there seems to be a greater possibility that raw oxidizer might escape under unusual conditions. On the other hand, its simplicity and apparent lack of sources of unreliability are in its favor, as is the fact that its reliable use seems to have been proven over many years, by various organizations.

The exact performance of the burner is very much an open question, in our opinion, as discussed in the preceding section. The only test results available were not quantitative, were the result of an apparently relatively modest effort, and in addition were such as to cause some doubt since neither CO nor NO were reported for fuel-rich runs. We want to emphasize, however, that while this result seems unlikely it is certainly not inconceivable, and could be a result of the more or less stratified nature of the burner's combustion zone, with fuel and waste oxidizer in the center and a second oxidizer - air - surrounding this region. It is possible that combustion here is sequential in nature, involving first N_2O_4 and excess fuel with air entering after complete N_2O_4 destruction but not too late to effectively oxidize the large amount of CO that must certainly form during primary combustion. Even so, however, some amount of nitric oxide formation seems inevitable.

At any rate, our conclusion of environmental acceptability is not based on any particular assumptions regarding NO or CO formation. Even if both are formed in relatively large amounts, the burner is a very significant improvement over atmospheric venting, which is itself not unacceptable under favorable atmospheric conditions. The flare burner converts what would be a dense, noxious reddish-brown plume into an essentially clean, invisible effluent. Given adequate dilution in an area free of pre-existing NO_x and CO problems, the effluent is relatively harmless. The difference between what we regard as its worst potential performance, and the performance reported in NASA TN D-3965, is essentially a difference between an acceptable disposal system and a thoroughly exemplary disposal system.

B. SCRUBBING - ABSORPTION IN WATER

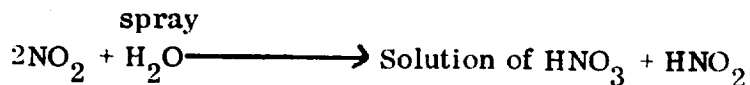
V.B.1. Current Applications

One of the organizations contacted during Phase 1 of this study pressurizes N_2O_4 vapors with nitrogen gas and sends them through a scrubber and thence to a system of holding ponds. Another organization captures N_2O_4 vapors by sparging through water drums. The contaminated water

is then reportedly shipped to the NASA facility at White Sands, New Mexico for disposal.

V. B. 2. Chemical Description

NO_2 vapors are relatively difficult to absorb in plain water and when absorbed form a strong acid:



V. B. 3. Environmental Standards

Applicable environmental standards are described and discussed in Section II. C., Chemical Treatment of Liquid Hydrazine, Section IV. B., Chemical Neutralization of Liquid N_2O_4 , and Section IV. C., Simple Dilution of Liquid N_2O_4 with Water.

V. B. 4. Overall Evaluation

Provided that effective scrubbing is accomplished, this method is essentially just a means of exchanging a vapor disposal problem for a liquid disposal problem. The liquid should then be disposed of either by chemical neutralization (see Section IV. B.) or by dilution with copious amounts of water (Section IV. C.). Evaluation of this disposal method is dependent on the ultimate liquid disposal method chosen; see the appropriate section for overall evaluation and restrictions.

C. SCRUBBING - ABSORPTION IN Na HCO_3

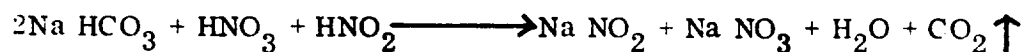
V. C. 1. Current Applications

Pad 17 at Cape Canaveral Air Force Station uses a 5% sodium bicarbonate scrubber when loading N_2O_4 .

V. C. 2. Chemical Description

Sodium bicarbonate is present as a water solution; NO_2 dissolves in

the water to form nitric and nitrous acid, as in other disposal processes, which in turn react with the bicarbonate to form nitrate and nitrite:



V.C.3. Environmental Standards

Applicable environmental standards are described and discussed in Section II. C., Chemical Treatment of Liquid Hydrazines, and Section IV. B., Chemical Neutralization of Liquid N_2O_4 .

V.C.4. Overall Evaluation

Provided that effective scrubbing is accomplished, this method is essentially identical to the sodium bicarbonate neutralization method described in IV. B. The overall evaluation, and a discussion in practical terms, are given at the end of that section.

This scrubbing method differs from the water scrubbing method of the preceding section in that it is more nearly an ultimate disposal method, since the N_2O_4 (and HNO_2 and HNO_3) are actually eliminated. Note, however, that copious dilution with water would still be required before the effluent could be discharged to public waters. Other means of disposal, however, might be feasible, such as evaporative ponds or controlled ground disposal.

A practical disadvantage to this method is the fact that formation of solid residues, nozzle plugging, and corrosion in bicarbonate scrubbers result in maintenance and reliability problems.

D. ATMOSPHERIC VENTING

V.D.1. Current Applications

One of the most common means of disposal of N_2O_4 over the years has been simple venting, or boil-off, to the atmosphere. Usually vent stacks

are relatively high, and meteorological precautions (primarily wind velocity and direction) are adhered to. In at least one instance, large fans are used to mix copious quantities of air with the oxidizer vapors and propel the mixture skyward. Incidents periodically occur, but they do not normally seem to be serious. One of the major disadvantages is the highly visible plume.

V. D. 2. Chemical Description

Nitrogen tetroxide dissociates to a very high degree when it evaporates:



The resultant nitrogen dioxide has been discussed extensively in earlier sections. Further reactions can occur in the atmosphere, including the formation of "acid rain",



Nitric oxide is slowly oxidized by oxygen, or rapidly oxidized by ozone, to form more nitrogen dioxide:



V. D. 3. Environmental Standards

Applicable environmental standards have been reviewed and discussed in the various sections treating incineration.

V. D. 4. Overall Evaluation

Since the TLV for NO_2 is 9 milligrams per cubic meter of air, dispersal of 480 gallons of N_2O_4 would require approximately 264,000,000 cubic meters to reduce concentrations to the TLV, or 100 times this volume to achieve one per cent of the TLV. This latter figure is a volume 10 kilometers square by 264 meters deep - not necessarily an unreasonably large volume, provided discharge rates are slow enough to allow adequate diffusion and mixing with this volume of air.

For this reason, we do not believe that atmospheric venting is inherently unacceptable. However, other factors must be considered, such as:

1. Variations in weather conditions, and their effect on mixing,
2. the possibility of local acid rains,
3. the assumption was made above that the surrounding air did not already contain significant NO_x concentrations. If future growth of any particular region causes increasing NO_x levels, individual sources will become more and more of a problem.

We therefore conclude that atmospheric venting is not an environmentally acceptable method of N_2O_4 disposal in terms of planned or future facilities, except in very special cases: very low vent rates, or very occasional venting requirements with no prospects for an urgent need to vent "on demand".

VI. DISPOSAL OF LIQUID IRFNA

A. GENERAL REMARKS

Type IIIA or type IIIB IRFNA contains $0.7 \pm 0.1\%$ HF by weight, along with $14 \pm 1.0\%$ of dissolved NO_2 . It has been estimated that the quantity of IRFNA waste disposed at ETR is under 200 gallons per year representing less than 2 gallons of HF (less than 15 pounds) per year. This relatively insignificant amount of pollutant could safely be discharged into a sewer or stream with simple water dilution.

It was reported that in one isolated incident a 1,500 gallon batch of IRFNA (used for metal passivation) was disposed of by water dilution and dumping into a lime pit.

B. INCINERATION

Pan American World Airways, Inc. Standard Practice Instruction # 41-26-013 (dated April 29, 1971) includes IRFNA in the incineration procedure because the characteristics of this oxidizer are similar to N_2O_4 . Inquiries revealed, however, that no IRFNA has ever been incinerated at this installation.

A review of all the contacts made during Phase 1 of this study also failed to reveal disposition of IRFNA by incineration. Therefore, we do not have any actual data from IRFNA incineration to evaluate this method or to predict the concentration of the combustion emission products with auxiliary fuels.

Threshold Limit Values established by ACGIH and OSHA are 2 ppm for HNO_3 vapors, 5 ppm for NO_2 , 25 ppm for NO, and 3 ppm for HF. It is our estimate that the NO and HF values would probably be greatly exceeded

in the effluent of any current state-of-the-art incinerator used to destroy IRFNA, although air dilution would alleviate the problem. See Section II. A., Incineration of Liquid Hydrazines, Section IV. A., Incineration of Liquid N_2O_4 , and Section V. A., N_2O_4 Flare Burners, for more detailed discussions of incinerators. In particular, the discussion in Section IV. A. of the specific limitations of incinerators with regard to destruction of oxidizers is equally applicable to IRFNA. The presence of HF in IRFNA is an added difficulty relative to N_2O_4 .

Because of the relatively higher boiling point (150°F at one atmosphere) of IRFNA compared to N_2O_4 (70°F) atomization of liquid into the incinerator/flare-burner rather than evaporation (as for N_2O_4) might be required to successfully decompose this oxidizer.

The effective use of incinerators for IRFNA has not been sufficiently demonstrated or tested so that they could be recommended. If a large quantity of IRFNA and N_2O_4 waste oxidizers were involved, this could be one specific area where additional research or development activity would be needed to bring current practice to an "adequate" level.

C. CHEMICAL TREATMENT*

Waste streams containing IRFNA are typically treated by neutralization/dilution procedures. In fact, diluting with water and/or neutralizing with a suitable alkali before discharging the effluent were the only current IRFNA disposal methods reported in Phase 1 of this study.

A brief description of the procedure follows. The waste IRFNA (diluted with sufficient H_2O , about 1:100, to keep the reaction within bounds) is collected into a suitable tank or pond. The solution is then treated with one of a number of reagents as given in Table XXI. The reagents are added slowly to allow heat dissipation, and in slight excess. A soluble calcium salt may be used with any of them, if desired, to precipitate the fluoride. If fluoride removal is desired a filtration or settling step is required. Then the neutralized solution is discharged. The pertinent equations are:

* Also see Appendix D

TABLE XXI
NEUTRALIZATION REAGENTS FOR IRFNA

Method	Neutralizing Reagent	Products Formed	Comments		
			Safety/ Inconspicuousness	Chemical Cost per lb IRFNA	Pollution
1	Na_2CO_3^- $\text{Ca}(\text{OH})_2$	Solution of NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, CO_2 , CaF_2 ppt	¹ Strong irritant ² Inconspicuous effluent	\$.055	Effluent may be corrosive and toxic due to nitrate and fluoride ions
2	NaOH	Solution of NaNO_3 , trace of HF	Same as above	\$.020	Effluent may be corrosive and toxic due to ni- trate & fluoride ions
3	NH_4OH	Solution of NH_4NO_3 , trace of HF	Same as above	\$.185	Effluent may be corrosive and toxic due to ni- trate & fluoride ions

1. $2\text{HNO}_3 + \text{Na}_2\text{CO}_3 \longrightarrow 2\text{NaNO}_3 + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
 $2\text{HF} + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaF}_2 \downarrow + 2\text{H}_2\text{O}$
 Filter, to Solid
 Waste Disposal
2. $\text{HNO}_3 + \text{NaOH} \longrightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
3. $\text{HNO}_3 + \text{NH}_4\text{OH} \longrightarrow \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$

There are only minor differences in the three methods shown in Table XXI for performing the chemical treatments. For example

1. In method (1) it is possible to remove the CaF_2 precipitate from the effluent by a filtration or settling step. It is also feasible to add a fluoride-precipitating agent in methods (2) and (3) for fluoride removal.
2. The care required in mixing and handling the strongly caustic NaOH solution is a slight disadvantage for method (2).
3. The odor of NH_3 may be objectional for method 3.
4. The Na_2CO_3 method has an advantage with respect to ease in handling.

Use of other neutralizing agents than those shown in Table XXI is also possible.

The effectiveness of the neutralization disposal method for IRFNA has been amply demonstrated over the years. The major disadvantages are the high chemical and equipment costs incurred in disposing of the waste IRFNA.

The effluent from the IRFNA treatment is both corrosive (several 1/10 of 1% HNO_3) and toxic (several hundred ppm HF). Copious dilution seems a logical and simple solution to the pollution requirement, provided ample water is available. The provisional Maximum Exposure Limits recommended in the TRW report¹ are 0.25 ppm for HNO_3 and 0.1 ppm for HF in water or soil. Disposing of one gallon of IRFNA by either the neutralization method or the dilution method requires approximately 10,000 gallons of water to reduce the NO_3^- concentration to the 100 ppm level. Concurrently the fluoride would be reduced to below the 1 ppm level. But to reduce the

¹Op. cit., Vol XII, page 105. Also see Table 5, Section 11.C of the present report.

NO_3^- to the provisional .25 ppm limit in water or soil would require approximately 4 million gallons of water; the HF to the provisional 0.1 ppm limit would require 100,000 gallons of water per gallon of IRFNA.

Disposal of the Ca F_2 precipitate should follow the guidelines established in the TRW report in connection with formation of the same waste product during treatment of plating, wash and tin recovery wastes from halogen tin lines used in tin plating:

"To allow economic recovery, the discharged, alkaline Ca F_2 slurry should be lagooned ... The separated Ca F_2 should then be dried, and re-used as metallurgical grade Ca F_2 in steel mill operations. Where economic recovery is not feasible, the sludge should be added to a landfill."²

Our evaluation of the neutralization disposal technique for IRFNA on the basis of products formed, safety of operation, inconspicuousness of effluent, cost of chemicals and pollution factors is that the three methods are all environmentally acceptable, and all essentially equivalent. Convenience or availability of chemicals would dictate the method to be used at any particular site. Ultimate disposal requires either copious dilution, as described above, or evaporation, with the solid residue used as fertilizer, as mentioned in Sections I and IV. B.

D. H_2O DILUTION

Water is the most easily used and the most readily available decontaminating agent. Smaller quantities of NO_x fumes evolve during dilution with H_2O than during treatment with the alkalies. Thus, simple dilution as a disposal method may be the preferable method for disposing of IRFNA rather than the more complicated and more expensive chemical neutralization method, provided HF does not constitute a major problem. Dilution can be made to meet the present and future environmental standards. The resulting product from IRFNA dilution is highly diluted NO_3^- solution. In contrast, the products from the neutralization reactions would

²Op. cit., Vol. XII, page 13.

be the same quantity of NO_3^- plus the added cations from the neutralizer. Provided that sufficient water is available, there is no limit to the amount of IRFNA that can be disposed of by the dilution method in a most expeditious manner; i. e. , it is suitable for disposal of small or large quantities of waste. Holding ponds containing much higher concentrations of wastes can be utilized as an alternative to direct stream disposal.

The environmental aspects of the resulting effluents from the dilution method are nearly the same as those in the preceding Section C, Chemical Treatment, and apply here as well. TLV's and provisional Maximum Exposure Limits are given in Section C.

One method for removing HF from waste effluents is by addition of a soluble calcium salt under controlled pH. The insoluble CaF_2 will precipitate out. This precipitate may be separated by filtration, settling or other suitable unit operation, and disposed of as described in the preceding section. A residual amount of CaF_2 (50 - 100 ppm) will remain in solution due to its slight solubility in water. It is only by further dilution with H_2O that the residual CaF_2 may be reduced to an acceptable level to conform to existing regulations. This precipitation was the subject of further work in Phase 3, and our experimental results are reported in the section on Application Studies.

Our evaluation of the dilution method for IRFNA disposal is that it is an environmentally acceptable method. It is simpler and more economical than the neutralization method, but the products formed, safety of operation, inconspicuousness of the effluent and pollution factors are approximately the same for both methods.

VII. DISPOSAL OF IRFNA VAPORS

A. INCINERATION

We were unable to find any user of IRFNA oxidizer who currently destroys the vapors by incineration. None of the correspondence received to date mentions this method of disposal for this material.

Part of the reason for this situation may be the higher boiling point (150 °F at one atmosphere) of IRFNA and significantly lower vapor pressure (5 psia @ 100 °F) than for N_2O_4 (70 °F at one atmosphere, 32 psia at 100 °F). Considerably less vapor is generated than for N_2O_4 . This results in, at most, a minor vapor problem and consequently little need for incineration of the vapors evolved during transfer operations as performed up to 1974. Forced or natural venting to atmosphere may provide adequate vapor dispersal.

In addition to resulting in lower absolute quantities of IRFNA vapors to be destroyed, the low vapor pressure of IRFNA at atmospheric temperature means that these vapors can only exist in mixtures containing noncondensable gases. (The "fumes", NO_2 , of course can be present separately; they are similar to the N_2O_4 vapors treated in Section V., and their disposal was covered in that section.) The special problems of incineration of vapors mixed with large volumes of essentially inert gases are discussed in Section III.A., Incineration of Hydrazine Vapors. In addition, the special problems of destruction of oxidizers by incineration are discussed in Section IV.A., Incineration of Liquid N_2O_4 , and V.A., N_2O_4 Flare Burners. Incineration of IRFNA would involve both these problems, although the noncondensable gases would be a relatively minor factor compared to their importance in the case of N_2H_4 .

It is possible that the Martin-Marietta flare burner described in Section V. A. would be a suitable means of destroying IRFNA vapors, probably with a certain amount of modification and developmental testing.

Threshold Limit Values established by ACGIH and OSHA for IRFNA vapors are: 2 ppm for HNO_3 , 5 ppm for NO_2 , and 3 ppm for HF. Also see Table XI, Section II. A., for the TLV's of the products of combustion.

Our overall evaluation is that this method is potentially acceptable, but cannot be recommended at this time. The problems involved in adapting existing burners to the destruction of an oxidizer mixed with large amounts of relatively inert gas might be considerable. Before this method can be considered environmentally acceptable, a fairly extensive test program to demonstrate emission levels would be required.

B. SCRUBBING

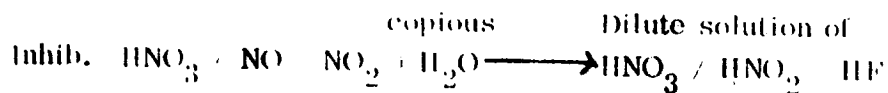
The scrubbing technique with plain water, solvent or dissolved reagent has been used successfully for years by industry as a disposal method for many gases, mists or particulates. For example, in the manufacture of HNO_3 , in the past few years stack effluents were on the order of 1500 to 3,000 ppm NO_x with the tell-tale brownish color. Attempts were made to reduce such concentrations to approximately 300 ppm, usually by resin absorption or catalytic combustion systems. The abatement equipment in this case costs from several hundred thousand to several million dollars for a large installation.

For a small installation plain water or alkaline solution scrubbing may be used to reduce the toxic gas emissions. These small units suffer from problems of low efficiency in terms of vapor absorption, and high operational and maintenance costs.

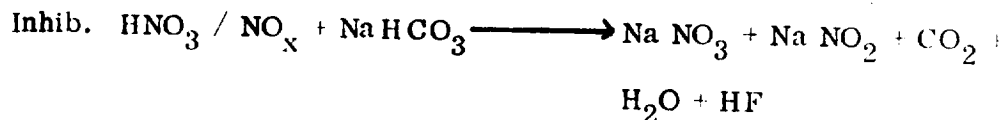
Regardless of the method used, water alone or alkaline solution, the amount of nitrate released will be the same, but the pH of the effluent solution is controlled in the case of alkali addition.

The scrubbing equations are:

1. with plain H_2O :



2. with NaHCO_3 solution:



Other alkaline reagents may be used in addition to the one shown in equation two.

Inquiries revealed that scrubbing IRFNA vapors is not presently carried out at ETR except for one small scrubber on the vent line of a 5000 gallon IRFNA storage tank.

Our overall evaluation is that scrubbing of IRFNA vapors is an environmentally acceptable disposal method. There is a question regarding constituent concentrations in the atmospheric discharge, but even if the scrubber is less than 100% effective it will represent a significant improvement over atmospheric venting, which is marginally acceptable for small quantities. The liquid discharge from the scrubber should be treated by either dilution or neutralization, as discussed in Sections VI.C. and D.

C. ATMOSPHERIC VENTING

Since the TLV for HNO_3 in air is 2 mg per cubic meter, dispersal of one gallon of IRFNA (85% HNO_3 by weight) would require approximately 2.5×10^6 cubic meters of air to reach the TLV. This is a relatively modest volume in terms of the air over one square kilometer of land. Nitrogen dioxide will be present in smaller quantities and has a higher Threshold Limit Value; HF will be present in much smaller quantities. As discussed in Subsection A. above, relatively small amounts of vent vapor per unit mass of liquid handled are expected in the case of IRFNA compared to N_2O_4 , with its much lower boiling point.

For these reasons, we do not believe that atmospheric venting of reasonably small quantities (or rates) of IRFNA is inherently unacceptable. However, because of other factors, such as varying atmospheric conditions, the possibility of pre-existing nitric acid or nitrogen dioxide atmospheric pollution, etc., we do not believe that atmospheric venting can be considered an environmentally acceptable option for future IRFNA disposal systems.

VIII. DISPOSAL OF LIQUID HYDROGEN PEROXIDE

A. CHEMICAL DECOMPOSITION

VIII. A. 1. Current Applications

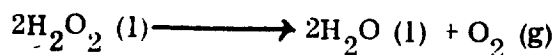
Concentrated hydrogen peroxide (in excess of 52% by weight) is a powerful oxidizing agent and rapid decomposition can be hazardous. However, neither the chemical industry nor the TRW study¹ recommends any procedures more elaborate than dilution with copious amounts of water, usually reported as 100:1. This is followed by simply pouring the solution on the ground, into a drainage system, or into the sewer system.

One organization has reported pouring laboratory quantities over a platinum or silver mesh to catalyze the reaction. Larger quantities were diluted with water to between 25% and 40% H_2O_2 and decomposed by catalyzing with caustic. At 100°C and a caustic level of 0.5 - 1 % Na OH, decomposition is 95% complete in one hour.

Several organizations have reported successfully disposing of hydrazines with the aid of H_2O_2 , and also used it for treating holding ponds.

VIII. A. 2. Chemical Description

Hydrogen peroxide is unstable and decomposes spontaneously according to the reaction:



with the liberation of approximately 47 kcal of heat at a reaction temperature of 20°C (25 kcal/mole - H_2O_2).

The mechanism and rate of decomposition depends on many factors including temperature, pH, and the presence of catalysts. In general, the

¹Op. cit., Vol. XII, pages 107-108.

rate increases with increasing pH. The rate increases approximately 2.2 times with each 10°C rise in temperature over the range 20°C - 100°C. The following table presents qualitative data for the temperature dependence.

<u>Temperature</u>	<u>Approximate Decomposition Rate</u>
30°C	1 % per year
66°C	1% per week
100°C	2% per day
140°C	Rapid, with boiling

VIII. A. 3. Environmental Standards

As noted above, the decomposition products of hydrogen peroxide are pure water and pure oxygen gas, so there is absolutely no environmental problem with disposal by decomposition of the compound. There are, however, some health hazards in handling the H_2O_2 in concentrated form. Contact with the liquid, mist, or vapor can cause irritation of the skin, eyes, and mucous membranes. Flushing the affected area with water is the only required treatment. The Threshold Limit Value (ACGIH-1969) for a 90% solution dispersed in air as aerosol is 1 ppm (1 mg/m^3). The provisional Maximum Exposure Limits recommended in the TRW report² are 0.014

²Op. cit., Vol. XII, pages 104-105.

mg m³ for H₂O₂ as a contaminant in air, or 0.07 ppm as a contaminant in water and soil.

VIII. A. 4. Overall Evaluation

Hydrogen peroxide presents the least disposal problem of any of the propellants under study, and presents virtually no pollution problems. In its pure state it contains no contaminants that would cause surface water pollution or interference with sewage (see B. 1. below). This would also hold true for the materials that would be considered contaminants in the H₂O₂ necessitating its disposal.

However, concentrated hydrogen peroxide solutions should be diluted with copious amounts of water before disposal to prevent strong reaction with organic materials, as discussed above. This dilution will also prevent injury to fish life since there is some evidence that high concentrations of H₂O₂ are, in fact, harmful to certain fish.³

One possible exception that may arise is the disposal of contaminated H₂O₂ that has been stabilized with H₃PO₄ (phosphoric acid). Decomposition would leave phosphate residues requiring additional treatment before disposal into bodies of water. This would depend, of course, on the total content of phosphates in the dilute solution.

A consideration of disposal techniques must include the hazards involved in handling. With regard to fire and explosion hazards the following quotes are extracted from "Chemical Safety Data Sheet SD-53", Manufacturing Chemists' Association:

" Hydrogen peroxide itself is nonflammable. However, it is a strong oxidizer, and if allowed to remain in contact with readily oxidizable organic materials, it may cause spontaneous combustion. In addition, hydrogen peroxide solutions are catalytically decomposed by many common materials such as heavy metals and their salts, ordinary dirt, ferments, enzymes, etc. liberating oxygen which will promote the burning of combustible materials.

" Practically all solid combustible materials contain sufficient catalytic impurities to decompose hydrogen peroxide rapidly.

³ "Treatment of Waste Waters Containing Hydrogen Peroxide, Hydrazine, and Methanol", Chemistry and Industry, 1951, pages 1104-6.

In concentrations above 65% H_2O_2 , there is insufficient water present or formed to remove the heat of decomposition by vaporization. The adiabatic decomposition temperature of 90% H_2O_2 , for example, is 740 °C. (1364 °F.) and combustible materials in contact with the decomposition products will quickly burst into flame.

" At ambient temperature, under normal conditions of storage it has been impossible to obtain a propagating detonation from commercially produced hydrogen peroxide.

" Contaminated hydrogen peroxide can decompose at a rate which will exceed the capacity of the vent on the container or tank to remove the decomposition products. This decomposition can be self-accelerating in high strength hydrogen peroxide because the rate of heat evolution may exceed the rate of heat loss from the container to the surroundings. If this process is permitted to continue, an explosive pressure rupture of the container will result.

" There is little possibility that hydrogen peroxide vapors in the explosive range will be generated under ordinary storage or handling conditions. Vapors in the explosive range can be reached in a fire or in experiments with high strength hydrogen peroxide. Explosive vapors can also be produced when hydrogen peroxide, in concentrations of 74%, or greater, is heated to its boiling point. "

The explosive hazards of hydrogen hydroxide are demonstrated in Figure 13, taken from the same source, where it is also evident that temperatures of concentrated H_2O_2 should be maintained below 110 °C to prevent the formation of an explosive gas over any solution. Decomposition properties are given in Table XXII, also taken from the same source.

The partial pressures of H_2O_2 and H_2O are comparable over 98% solutions at 30 °C. At 70% the partial pressure of H_2O_2 is an order of magnitude lower than that for water and at 30% it is two orders of magnitude less (Table XXIII). One would conclude that dilute solutions would be substantially decomposed and not give off substantial quantities of H_2O_2 vapors.

From this information we conclude that there are no insurmountable difficulties in either storage or handling this propellant. Disposal by simply allowing the material to decompose in holding ponds is quite satisfactory, perhaps employing agitation to accelerate the decomposition process.

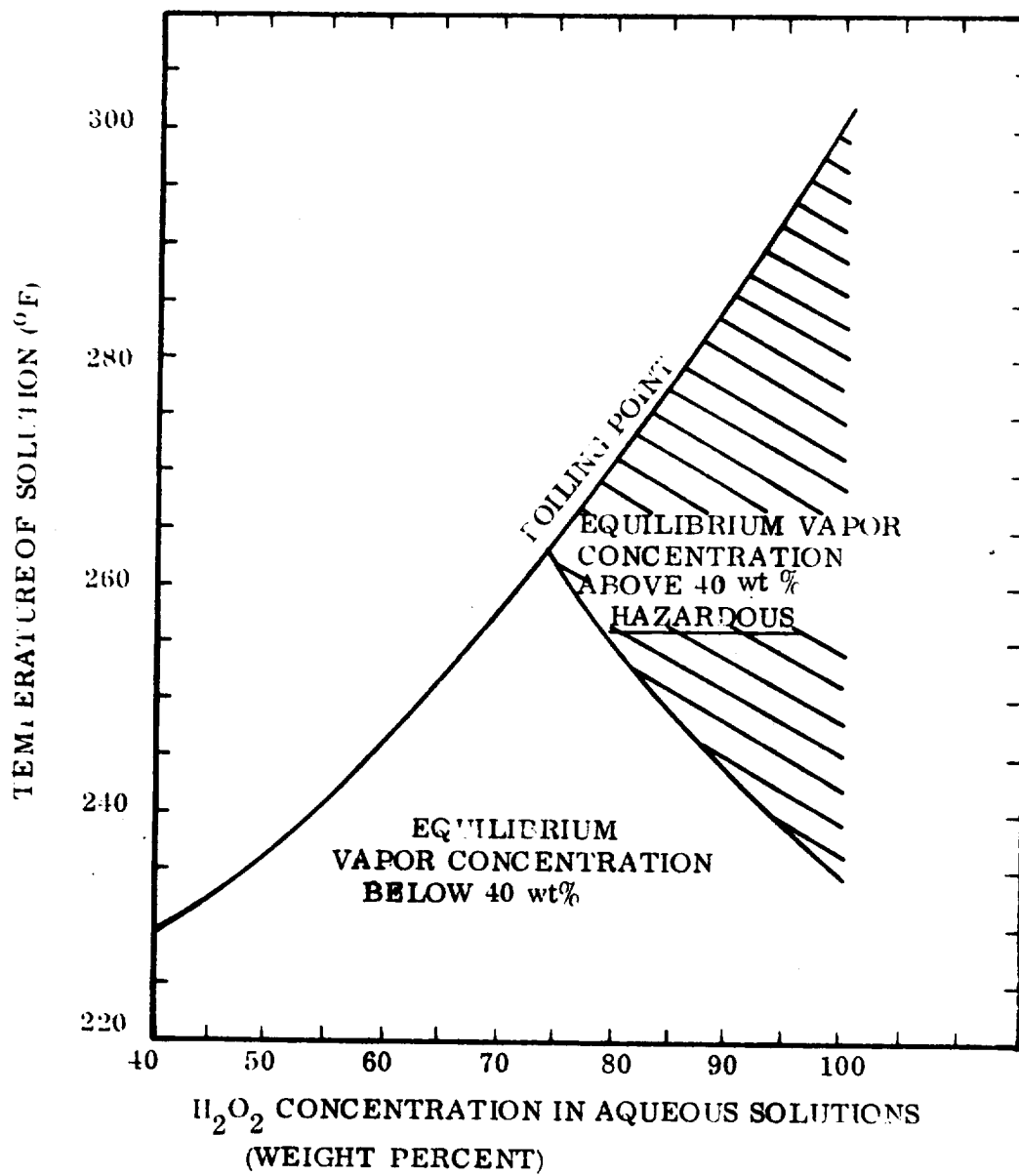


FIGURE 13

TEMPERATURES FOR FORMATION OF EXPLOSIVE GAS OVER
H₂O₂ - WATER SOLUTIONS AT ONE ATMOSPHERE PRESSURE

TABLE XXII
DECOMPOSITION PROPERTIES OF HIGH STRENGTH HYDROGEN PEROXIDE

Weight % H_2O_2	Adiabatic Decom- position Temper- ature °C.	Heat of Decom- position BTU/lb. of Solution at 20 °C.	Volume of Decom- position Gases Cu. Ft. / Cu. Ft. of Solution at 20 °C.	Volume of Decom- position Gases Cu. Ft. / lb. of Solution at 20 °C.
70	233	850	2545	32
80	487	980	3870	46
90	740	1110	5233	60
100	996	1240	6643	73

TABLE XXIII
PROPERTIES OF HYDROGEN PEROXIDE SOLUTIONS

H ₂ O ₂ Content, Weight	30%	35%	50%	70%	90%	98%
Active Oxygen, % weight	14.1	16.5	23.5	32.9	42.3	46.1
Boiling point, C.	106.2	107.8	113.9	125	141	148.6
F.	222	226	237	258	286	299.5
Density, 20 °C., g./ml.	1.11	1.133	1.196	1.29	1.387	1.436
lb./gal.	9.26	9.44	9.98	10.7	11.6	11.95
Freezing point, °C.	-26	-32.8	-50	-39	-11	-2.5
°F.	-14.8	-27	-58	-38	12	27.5
Vapor pressure, 30 °C., mm. Hg.						
Total pressure (H ₂ O ₂ and H ₂ O)	24	23	18	11	5	3
Partial pressure (H ₂ O ₂)	0.27	0.36	0.74	1.5	2.5	2.7
Threshold Limit (ACGIH - 1968)	1 ppm -- applicable to all strengths.					

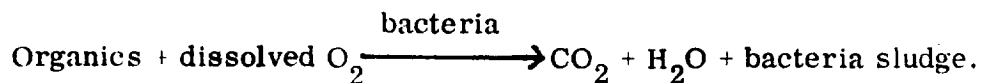
B. BIOLOGICAL DISPOSAL

VIII. B. 1. Current Applications

The use of H_2O_2 as a source of supplemental oxygen has been successfully demonstrated by DuPont for several prevalent problems in both industrial and municipal waste treatment systems.¹

VIII. B. 2. Chemical Description

Biological decomposition of H_2O_2 provides an additional form of oxygenation or aeration to satisfy metabolic requirements of microorganisms. The reactions are:



VIII. B. 3. Environmental Standards

Environmental standards are the same as described in Subsection A.3. above.

VIII. B. 4. Overall Evaluation

One obvious criticism of this form of disposal of waste H_2O_2 is the uncertainty in supply. However, Haskins points out that what is often needed is a substitute source of oxygen that can be intimately mixed with the water and organisms that does not require elaborate equipment. Further, these oxygen sources only need to be available to meet emergency or short term needs. For example, problems related to oxygen capacity of the aeration system are generally sporadic, due either to mechanical failures or organic

¹James W. Haskins, Jr., " H_2O_2 Looks Good for Sewage Treatment", Innovation, Fall 1973, pages 6-9 (E.I. DuPont de Nemours and Company., Inc., Wilmington, Delaware 19898).

spills. For problems requiring plant modifications, EPA and State standards could continue to be met while modifications are made. Equipment requirements are quite minimal - a drum of H_2O_2 with a metering pump.

Presently, cost is perhaps the only disadvantage to the use of H_2O_2 relative to air as a supplemental source of oxygen, but because of its advantages (i.e., ease of handling, low equipment investment, and excellent O_2 transfer capabilities), H_2O_2 may be the only practical means of solving the problem in many cases. We conclude that this is an ideal means of disposing H_2O_2 in drum quantities from both an economic and ecological standpoint.

For large as well as small quantities of H_2O_2 , draining into lakes, ponds, or streams under proper controls would be an acceptable method of disposal. The H_2O_2 would kill the anaerobic bacteria, a major source of infectious disease, and the liberated oxygen could be beneficial for aquatic life. Dilute solutions would be required, however, since there are indications that greater than 1% solutions could be toxic to fish. More concentrated solutions would necessitate metering apparatus. This could be the most economical means of disposal and also be ecologically beneficial.

C. POURING ON THE GROUND

Preferably, waste hydrogen peroxide should first go to a holding pond before discharging to an open body of water or a drainage ditch containing water. Because of the presence of oxidizable organics in the soil it is recommended that the practice of pouring on the ground be employed only in case of emergency spills, and then the area should be flushed with large volumes of water and care employed to avoid immediate dumping into streams.

IX. DISPOSAL OF H_2O_2 VAPORS

A. ATMOSPHERIC VENTING

Again, we point out that the decomposition products are harmless and that H_2O_2 itself is not toxic, save for irritation to skin and mucous membranes.

In light of previous discussion on decomposition rates and products and considering the rate at which the vapors will disperse, we conclude that straight venting of H_2O_2 vapors to the atmosphere is quite satisfactory.

ALTERNATIVE DISPOSAL CONCEPTS (PHASE 3)

	Page
I. Introduction	162
II. Vapor Condensation	164
A. The removal of a condensible constituent from a mixture of gases - temperature and energy considerations	165
B. Condensation of N_2O_4 - NO_2 vapors	185
C. Distillation and steam scrubbing of monomethyl hydrazine	190
III. Destruction of N_2H_4 , MMH or N_2O_4 by Gamma Irradiation	196
IV. Catalytic Decomposition	202
V. Calcium Carbonate as a Neutralization Agent for N_2O_4	207
VI. Vapor Phase Addition of N_2O_4 to Holding Ponds	211
VII. Oxidation of Diluted N_2H_4 by Ozone Bubbling	216

I. INTRODUCTION

This first category of studies undertaken as part of Phase 3 involved disposal concepts that are not currently in use, that were deemed promising as alternatives to current concepts. Especial emphasis was given to concepts applicable to vapor phase disposal, because of the generally lower ratings given vapor phase concepts during Phase 2 and smaller selection of acceptable concepts available for vapors. Emphasis was also given to N_2O_4 disposal concepts, because of the fact that N_2O_4 does not eventually decompose in the presence of air or bacteria to form harmless substances as do the hydrazines.

Concepts studied included the following:

1. Vapor condensation. This concept is applicable for vapors of hydrazines as well as nitrogen tetroxide. Both experimental and theoretical studies were undertaken, with extremely favorable results. A variation on this method involves combined recondensation and steam scrubbing; tests run with MMH were very successful.

2. Gamma irradiation. This concept is applicable to water solutions of the hydrazine fuels and could therefore be used for both liquid disposal and scrubber discharge treatment. It is of interest primarily in conjunction with holding ponds, although other applications might be possible. Experimental results were quite favorable.

3. Catalytic decomposition. This concept appears feasible for all of the propellants of interest except IRFNA, with hydrogen peroxide posing the least problem and N_2O_4 probably the most difficulty. It is applicable to both liquid and vapor phases. It is probable that in the case of N_2O_4/NO_2 , catalytic decomposition of the vapor phase is closer to operational feasibility than liquid phase decomposition. Our efforts in this area did not go beyond a paper study; it is our conclusion that a fairly extensive research and development program will be necessary before a definitive statement regarding the feasibility, practicality, and economics of this concept can be made.

4. Calcium carbonate neutralization. This concept is applicable to water solutions of both N_2O_4 and IRFNA. An experimental study established

the feasibility, and verified the substantial benefits this concept has over neutralization concepts that rely on water soluble neutralization agents.

5. Vapor phase addition of N_2O_4 to holding ponds. The concept is applicable to N_2O_4 vapors, and possibly to the vapors of the other propellants as well. An experimental program established the feasibility of this concept for one type of bubbler design. Very small bubbles are probably essential; a thorough study of bubble size and pond depth requirements has not been performed. The practicality of this method, and its economic advantage or disadvantage relative to a scrubber, will depend on pumping requirements and the length of duct needed, which will vary according to the specific application.

6. Ozone oxidation. This concept is applicable to water solutions of hydrazine fuels. An experimental program showed that very rapid oxidation to very low concentrations is possible, with controllable temperature rise and negligible environmental impact. The method was judged to be entirely acceptable; whether it is desirable relative to the very similar, but cheaper, aeration methods is a question that would have to be answered in terms of any given application.

Other potential alternate disposal concepts came to our attention during the course of this study. Electrolytic chlorine generators, such as the units being installed in many residential swimming pools, offer a source of chlorine for neutralization without many of the undesirable qualities of the chlorine compounds currently being added to holding ponds; for large scale neutralization, it is likely that salt water will be required for the holding pond rather than fresh water. Magnesium hydroxide scrubbers for removal of NO from stack gases and formation of saleable by-products were described by Esso engineers at an AIChE meeting in 1970. Neither of these concepts were included in this study, and therefore they are not discussed in the following sections.

II. VAPOR CONDENSATION

Three tasks relating to vapor condensation were performed, as described in the following pages. First is a theoretical and numerical study of the removal - by cooling - of a condensible constituent from a mixture of gases. This problem is the important one for us, since vent gases will normally be at a temperature below the saturation temperatures of all the hypergolic propellants (for the pressures involved), and hence these propellants can be present as vapors only if mixed with other gas - that is, the propellants can only be above saturation if their partial pressures are substantially below the propellant tank pressures. The second task was an experimental study of the condensation of N_2O_4/NO_2 vapors, and the third was an experimental study of the condensation of MMH vapors. In this last investigation the concurrent use of steam scrubbing, to more positively preclude hydrazine release to the environment, was also included.

A. THE REMOVAL OF A CONDENSIBLE CONSTITUENT FROM A MIXTURE OF GASES - TEMPERATURE AND ENERGY CONSIDERATIONS

II. A. 1 Formulation

Consider the transfer of heat away from a gas mixture for the purpose of condensing one constituent, "C". If the mixture is in equilibrium at each instant in time, with all constituents assumed to be perfect gases, then the mole fraction of C is related to its partial pressure according to

$$\chi_c = \frac{p_c}{p_m}$$

where p_m is the mixture pressure, assumed constant. Hence the change in χ resulting from a change in its partial pressure is

$$d\chi_c = \frac{dp_c}{p_m} \quad (1)$$

The mole fraction of constituent C is related to its mass and molecular weight, m_c and M_c , and the mass and molecular weight of the non-condensable fraction, m_N and M_N , according to

$$\chi_c = \frac{\frac{m_c}{M_c}}{\frac{m_c}{M_c} + \frac{m_N}{M_N}} \quad (2)$$

and solving for m_c gives

$$m_c = \frac{M_c}{M_N} \left(\frac{\chi_c}{1 - \chi_c} \right) m_N \quad (2')$$

Since the molecular weight and the mass of the non-condensable constituents are all constant, we have

$$dm_c = \frac{M_c}{M_N} \left[\frac{d\chi_c}{(1 - \chi_c)^2} \right] m_N$$

and substituting for χ_c , $d\chi_c$ from equations (1) and (2) gives the result

$$dm_c = \frac{M_c M_N}{p_m m_N} \left(\frac{m_c}{M_c} + \frac{m_N}{M_N} \right)^2 (dp_{SAT})_c \quad (3)$$

where $p_{SAT}(T_m)$ for constituent C is assumed known, T_m being the mixture temperature. Equation (3) will be used as a difference equation to establish numerical relationships between m_c and T_m for various cases of interest.

The amount of energy that must be removed from this mixture of gases to accomplish an infinitesimal temperature change dT_m is

$$dQ = \left[m_N c_{pN} + m_c \left(\frac{dh_c}{dT} \right)_{SAT} \right] dT_m + (h_{fg})_c dm_c \quad (4)$$

where the specific heat, c_{p_N} , and latent heat, h_{fg} , are functions of T_m in the general case. $\left(\frac{dh_c}{dT}\right)$ is the rate of change of the enthalpy of C due to moving along the saturated vapor curve, and is also a function of T_m .

II.A.2. Initial Condition

Equation (2'), with $m_N = m_m - m_c$, becomes (after solving for m_c):

$$m_c = \frac{\frac{M_c}{M_N} \chi_c}{1 + \left(\frac{M_c}{M_N} - 1\right) \chi_c} m_m$$

where m_m is the total mixture mass, and

$$\chi_c = \frac{p_{SAT}}{p_m}$$

Similarly,

$$\begin{aligned} m_N = m_m - m_c &= m_m \left[1 - \frac{\frac{M_c}{M_N} \chi_c}{1 + \left(\frac{M_c}{M_N} - 1\right) \chi_c} \right] \\ &= \frac{1 - \chi_c}{1 + \left(\frac{M_c}{M_N} - 1\right) \chi_c} m_m \end{aligned}$$

These values for m_c and m_N were used in Equation (3) as initial values at the beginning of the finite difference procedure.

II. A. 3 Application to the Condensation of Hydrazine Vapors from Vent Gas

The method of analysis outlined above depends on knowledge of the saturated liquid-vapor $p - T$ relationship for constituent C. For the sake of computation, either a numerical (including graphical) or algebraic relationship is satisfactory.

In the case of the hydrazine types of interest, the following algebraic relationships were established by investigators working in the early days of rocketry under the sponsorship of the Bureau of Mines and Office of Naval Research (p in mm Hg, T in $^{\circ}\text{K}$):

¹
For N_2H_4 ,

$$\log_{10} p = 7.80687 - 1680.745/(T - 45.42) , \quad (5a)$$

²
For MMH ,

$$\log_{10} p = -7.88 \log_{10} T - 3146.0/T + 31.746 , \quad (5b)$$

³
For UDMH ,

$$\log_{10} p = -2717.132/T - 6.745741 \log_{10} T + 28.000194. \quad (5c)$$

¹ D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, "Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions." J. Am. Chem. Soc. 71, 2293 - 97 (1949).

² J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, "The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures, Entropy, and Thermodynamic Functions of Methylhydrazine." J. Am. Chem. Soc. 73, 1939 - 43 (1951). Note: the equation as published contains a misplaced decimal point in one term; this error was corrected in the equation written above to yield agreement with the experimental data published in the paper.

³ J. G. Aston, J. L. Wood and T. P. Zolki, "The Thermodynamic Properties and Configuration of Unsymmetrical Dimethylhydrazine." J. Am. Chem. Soc. 75, 6202 - 04 (1953).

All of these relationships were based on laboratory measurements, and are believed to result from establishing the empirical constants in theoretical thermochemical equations by least-squares fitting to the measured data. Plots of these equations are presented in Appendix A.

Data for the temperature dependence of h_{fg} and $(\partial h / \partial T)_{SAT}$ is not available, as far as we have been able to ascertain, except for a limited amount of data in the case of MMH. Theoretical approximations could certainly be obtained for the temperature dependence of h_{fg} using Clapeyron's equation and empirical equations of state; because of the relatively small temperature range of interest in this investigation, however, it was decided to treat h_{fg} and $(\partial h / \partial T)_{SAT}$ as constants.

The values of h_{fg} for N_2H_4 , MMH, and UDMH reported in the same references just quoted are 10,700, 9648, and 8366 cal/mole, respectively, at 298.16°K. In the case of the substituted hydrazines these are measured values, while for N_2H_4 it is a theoretical value based on the vapor pressure measurements, using the Berthelot equation of state and critical point data. In the latter case the estimated uncertainty is given as ± 75 cal/mole. Because this temperature (equal to 77° F) is an appropriate one for our vent gas application, these values were used as constant approximations to h_{fg} throughout the temperature range of interest.

The term $(\partial h / \partial T)_{SAT}$ can be expressed as a function of more easily obtainable quantities using the expansion

$$\left(\frac{\partial h}{\partial T}\right)_{SAT} = \left(\frac{\partial h}{\partial T}\right)_p + \left(\frac{\partial h}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_{SAT}$$

where all terms are functions of position along the saturation line, and $(dp/dT)_{SAT}$ can be obtained from equations (5a), (5b), or (5c), as appropriate.

For the sake of this investigation, the perfect gas assumption was made so that

$$\left(\frac{\partial h}{\partial p}\right)_T = 0$$

and the expression for $(dp/dT)_{SAT}$ was not needed. In the more general case, $(\partial h / \partial p)_T$ could be calculated from data for the specific volume of saturated vapor (or an equation of state) using the relation

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_p,$$

which is derived from Maxwell's equations.

In addition, it was further assumed (as in the case of h_{fg}) that the specific heat, $c_p \equiv (\partial h / \partial T)_p$, is constant throughout the temperature range of interest. Similarly, the temperature dependence of the specific heat of the non-condensable gas, c_{pN} , is also neglected.

With these assumptions, equation (4) becomes

$$dQ = (c_{pN} m_N + c_{pC} m_C) dT_m + (h_{fg})_C dm_C, \quad (4')$$

with m_N , c_{pN} , c_{pC} , and $(h_{fg})_C$ all being constants. The equation in this form was used as a finite difference equation in the computer code for this investigation.

Values for the specific heat c_{pC} were published for N_2H_4 by Scott et al.⁴, and for MMH by Aston et al.⁵. The values given at 298.16°K were 12.6 and 17.0 cal/deg/mole, respectively, and these values were chosen for the constants in equation (4'). In both cases these were the lowest temperatures for which vapor phase specific heats were given. Data for UDMH have not been found; on the basis

⁴See footnote 1 above

⁵See footnote 2 above

of the data above, and published data for the heat capacity of liquid UDMH, MMH, and N_2H_4 in the temperature range of interest, a guess of 22 cal/deg/mole for the specific heat of UDMH in the temperature range of interest was made and this value used in equation (4').

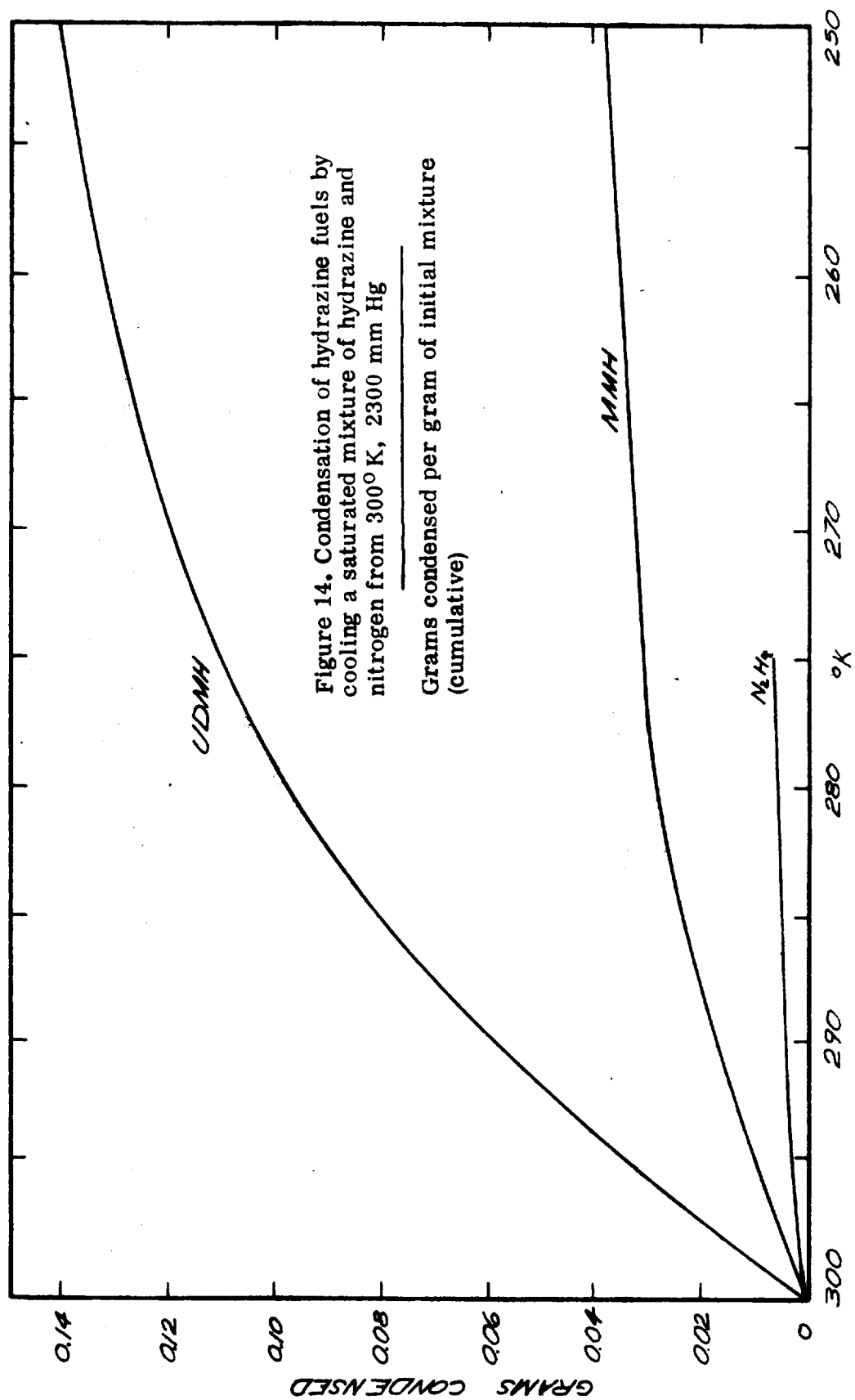
The vent gas was assumed to be nitrogen gas, saturated with N_2H_4 , MMH, or UDMH, at approximately three atmospheres pressure and atmospheric temperature. (This represents the maximum quantity of hydrazine that can be present in equilibrium as a vapor, since the normal state of all three hydrazines is liquid at these conditions.) The specific heat of nitrogen, c_{pN} in equation (4'), was taken to be 6.95 cal/deg/mole throughout the temperature range of interest.

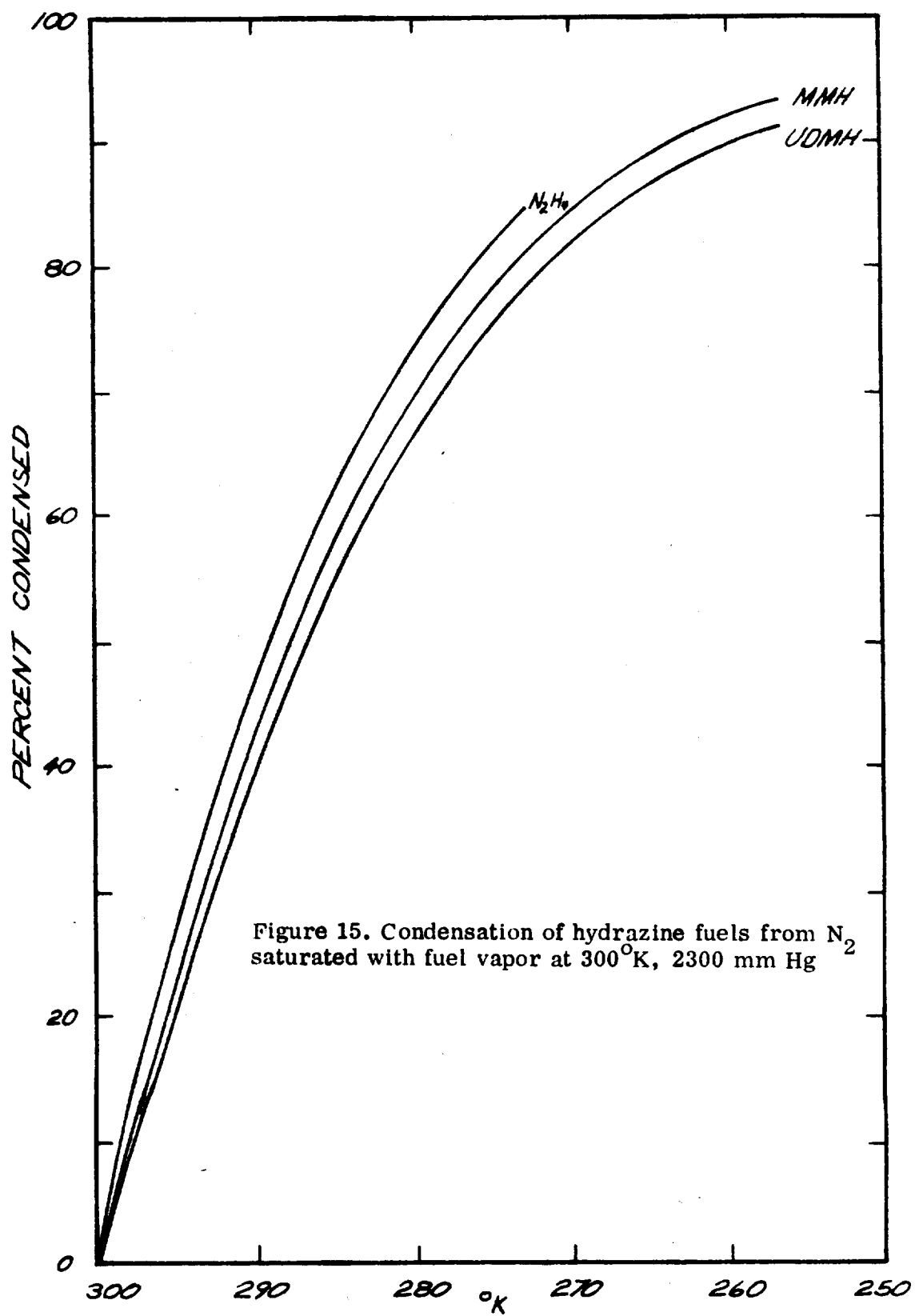
II. A. 4. Results for Hydrazine Condensation ;

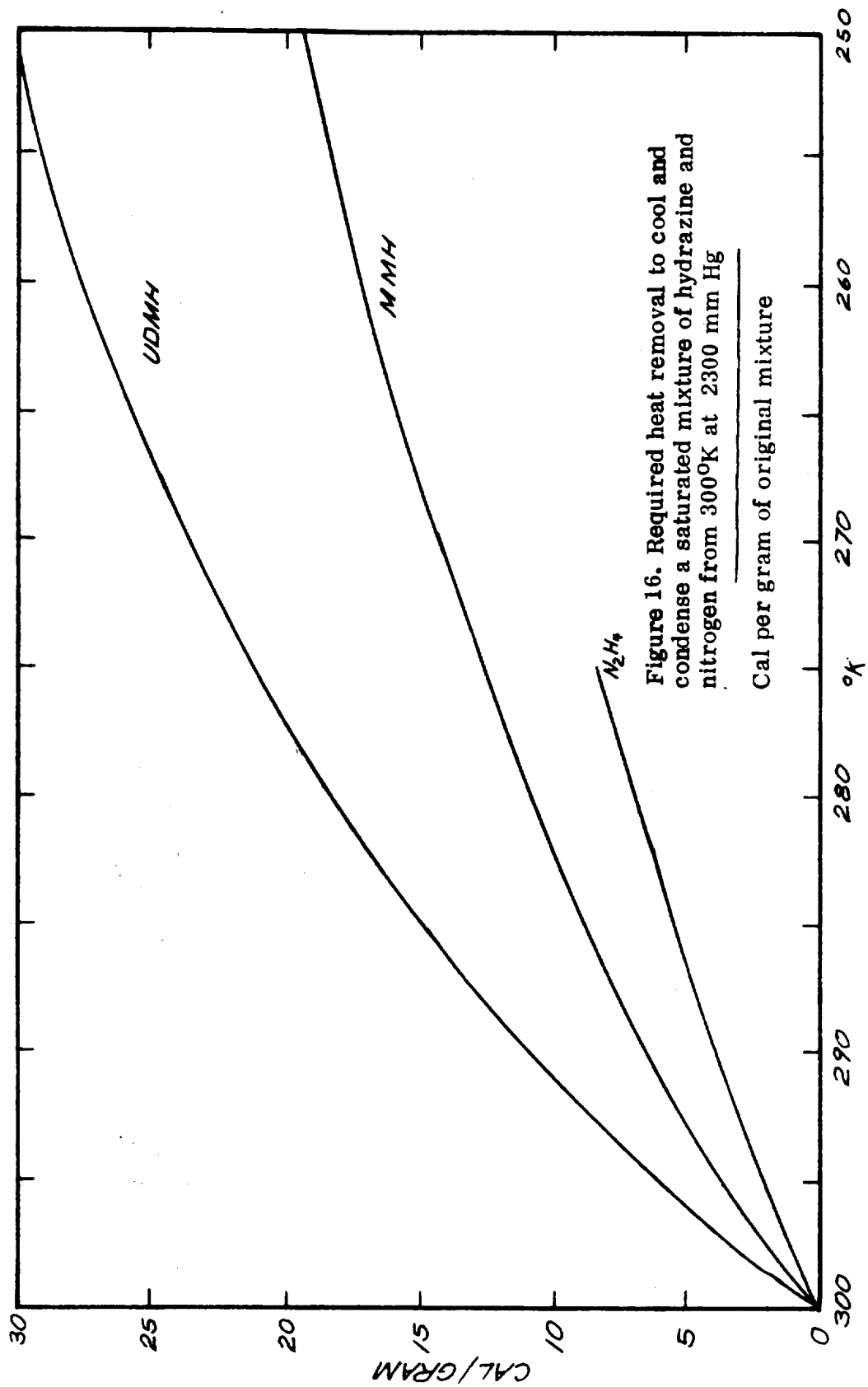
The computer code described above was used to investigate a case in which a saturated mixture initially at 300 °K, 2300 mm Hg, was progressively cooled.

Figure 14 shows the actual amount of hydrazine condensed, as a function of temperature. The large differences between UDMH, MMH, and N_2H_4 reflect the different amounts of fuel vapors initially present; UDMH, because of its relatively low boiling point (high vapor pressure), is initially present in large quantity, whereas N_2H_4 with the highest boiling point and lowest vapor pressure, is present in the vent gas in only very limited quantities. Figure 15 presents the same information, but in terms of percentages of the initial fuel mass condensed at any point during the process, rather than actual mass condensed. Here the three curves are much closer together, with N_2H_4 looking most favorable by a small margin. The N_2H_4 curves all terminate at the freezing point.

Figure 16 shows the heat removal required to achieve any given temperature. As in Figure 14, the UDMH curve is highest because of the relatively large amount of UDMH initially present. This







information is combined with the results for mass condensed in Figures 17 and 18, which show the "cost", in terms of heat removal per unit mass condensed, of condensing these fuels. Figure 17 shows overall heat removal divided by overall mass condensed for each fuel, while Figure 18 shows the incremental cost - calories per gram for the incremental mass of fuel condensed at any temperature. In these plots it is evident that recovery of UDMH is the most attractive of the three fuels, in terms of costs (both operating and equipment costs) per unit mass of fuel recovered.

To further define the cost, note that

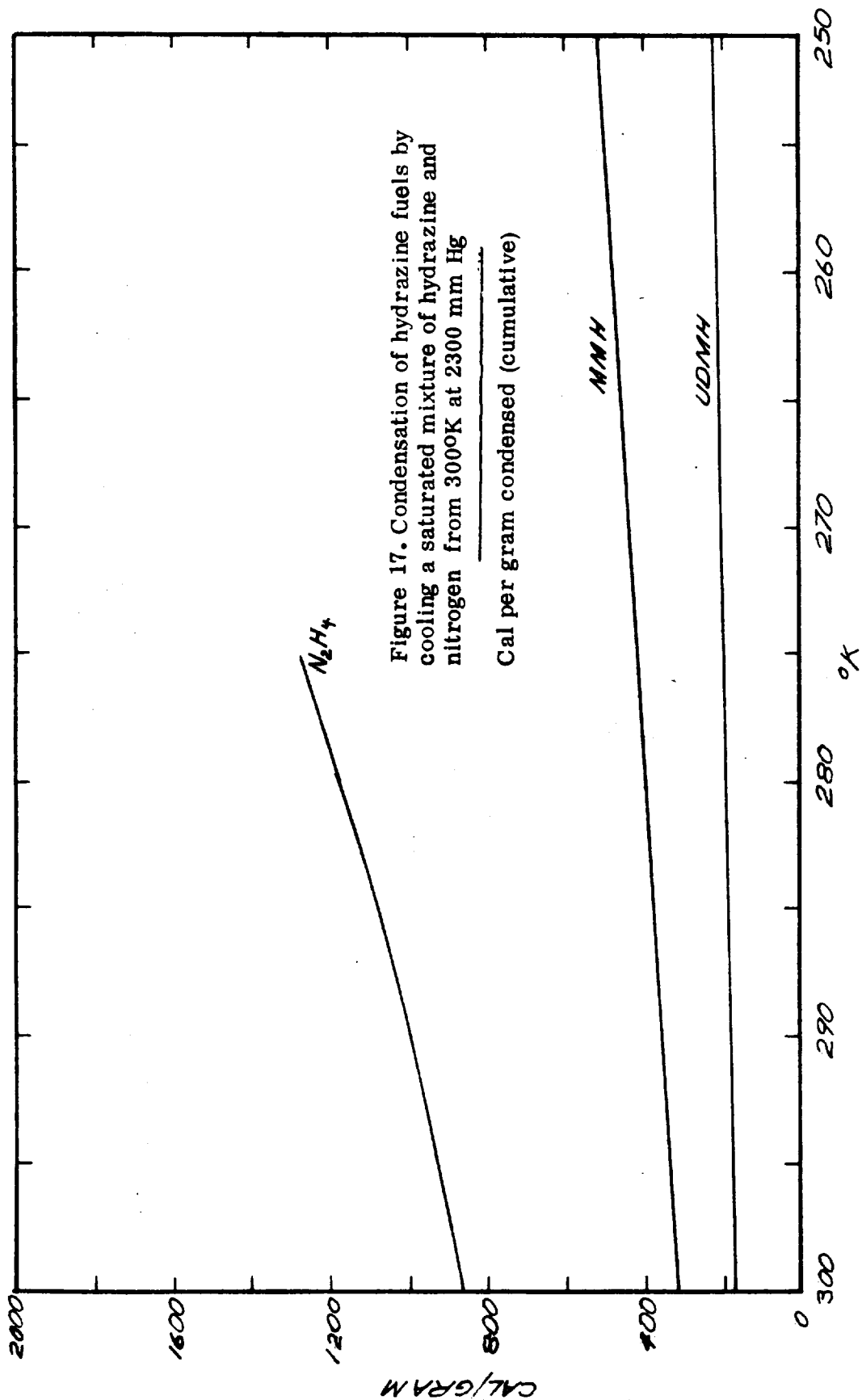
$$1 \frac{\text{cal}}{\text{gram}} = .0005274 \frac{\text{kw-hr}}{\text{lbm}}$$

so that the first UDMH condensed requires .0923 kw-hr of energy removal per pound recovered, the first MMH requires .1735 kw-hr per pound and the first N_2H_4 requires .458 kw-hr per pound. Similar figures at the point when 80% of the original fuel vapors are condensed are .1382, .349, and 1.292, respectively. If we assume that a refrigeration system with a coefficient of performance of 3 is used, and that electrical costs are 3 cents per kw-hr, then these figures also represent the electrical cost in pennies per pound of propellant recovered - modest figures even in the worst case. Capital equipment costs are of course not included.

II. A. 5. Application to the Condensation of Nitrogen Tetroxide Vapors from Vent Gas, and Results

The method of analysis was also applied to $\text{N}_2\text{O}_4/\text{NO}_2$ condensation. In this case an empirical equation, similar to equations (5a), (5b), and (5c) for the hydrazines, was presented by Giaque and Kemp⁶ for the vapor pressure of liquid nitrogen tetroxide in the range 261.90 to 294.9 °K:

⁶Giaque, W. F. and J. D. Kemp, "The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $\text{N}_2\text{O}_4 = 2\text{NO}_2 = 2\text{NO} + \text{O}_2$." J. Chem. Phys., Vol. 6, pp. 40 - 52 (1938).



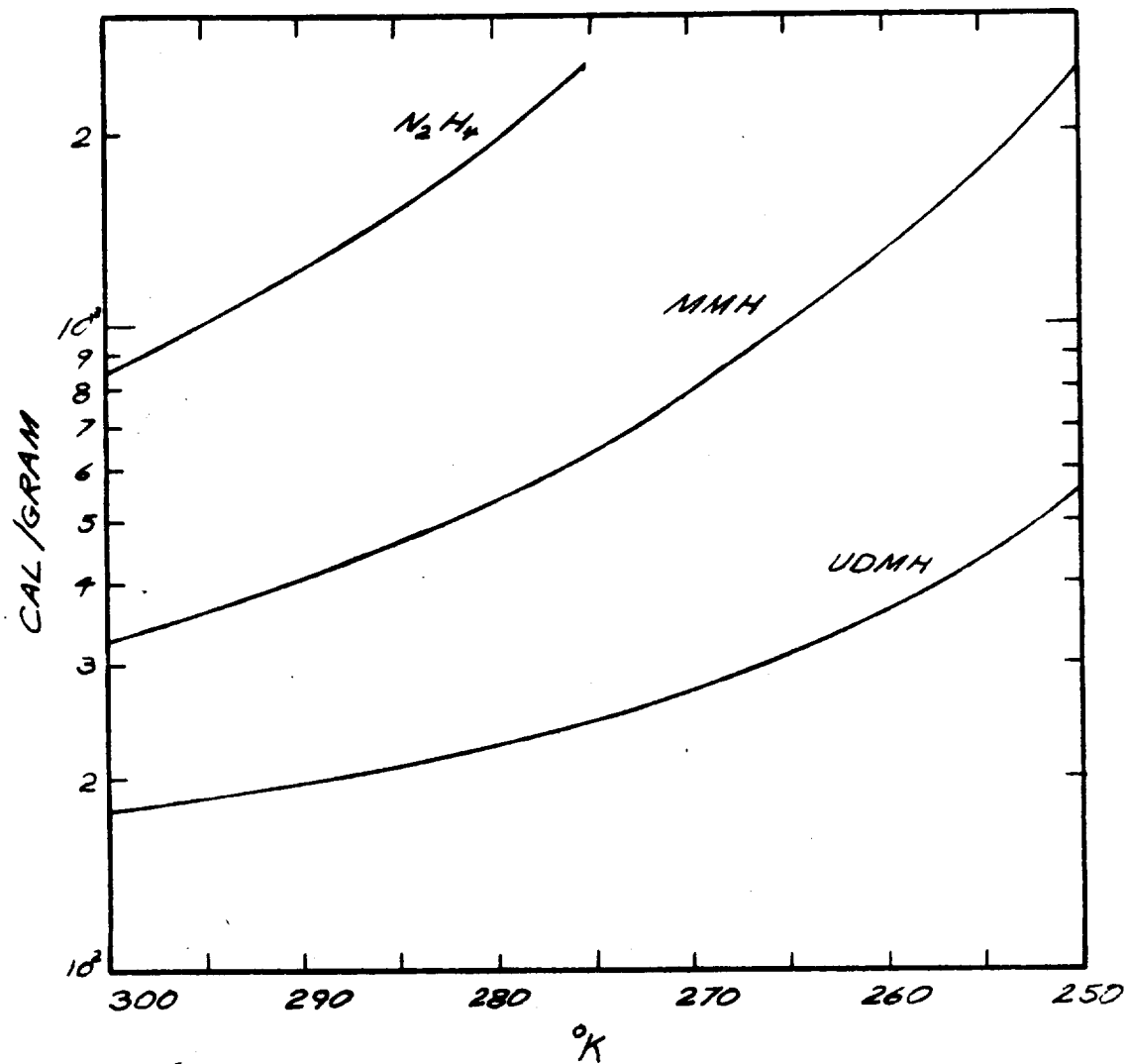


Figure 18. Condensation of hydrazine fuels by cooling a saturated mixture of hydrazine and nitrogen from 300°K at 2300 mm Hg

Cal per gram condensed (incremental)

$$\log_{10} p = -1753.000/T + 8.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6} T^2. \quad (6)$$

This equation was entered into the computer code described above, and is plotted in Appendix A. It should be noted that "these two substances (N_2O_4 and NO_2) are present at appreciable mole fractions under all conditions of equilibrium between the liquid and gaseous states,"⁷ and that this equation refers to the equilibrium mixture at any value of (p, T).

The latent heat of vaporization, h_{fg} , at 294.25°K was presented by Giauque and Kemp⁸ as 9110 ± 9 cal./mole, based on a series of several experiments. This value was compared with a theoretical value (based on empirical equations of state and degree of dissociation) of 9223 cal./mole. The value 9110 was used for this study. In using this value, "per mole" actually means per 92.016 grams, as if none of the N_2O_4 were dissociated. The value is nevertheless the actual equilibrium value. It should be noted that the equilibrium at the boiling point is not altered by the phase change - it is the same in the liquid and the vapor phases.

$(\partial h/\partial T)_{SAT}$ was approximated by c_p , as in the hydrazine cases. This specific heat was studied quite thoroughly by Fan and Mason⁹, who developed an extremely complex equation for the equilibrium heat capacity of the N_2O_4 - NO_2 - NO - O_2 system, taking account of the equilibrium reaction heat capacity. Numerical solutions were also presented; at 300°K, 1 atm the result was

$$c_p = 1.309 \text{ calories/gram } ^\circ K,$$

the value used in this study. It should be noted that this value is quite different from the frozen equilibrium heat capacity, which was also calculated by Fan and Mason. This value was found to be 0.2033 cal/g-°K, close to the value of approximately 0.235 cal/g-°K indicated by a curve

⁷Op. cit., p. 41.

⁸Op. cit., p. 45.

⁹Fan, S.S.T. and D.M. Mason, "Properties of the System $N_2O_4 = 2NO_2 = 2NO + O_2$." Journal of Chemical and Engineering Data, Vol. 7, pp. 183-186 (1962).

for NO_2 alone that was published in a very recent paper by Yaws and Hopper¹⁰. Whether equilibrium or frozen equilibrium is closer to reality in our situation is difficult to determine and of course depends on rates, etc. The equilibrium value was chosen as being the more conservative.

The molecular weight was found using the equilibrium constant data presented by Giaque and Kemp for the reaction $\text{N}_2\text{O}_4 = 2\text{NO}_2$. These data (which include experimental results obtained by several earlier investigators) can be very closely approximated by the linear relation

$$\log_{10} K = -11.585 + .036 T,$$

T being the temperature in $^{\circ}\text{K}$ and K the equilibrium constant in atmospheres. Having calculated K, the degree of dissociation, α , is calculated by the usual relation

$$\alpha = \left(\frac{K}{4p + K} \right)^{\frac{1}{2}},$$

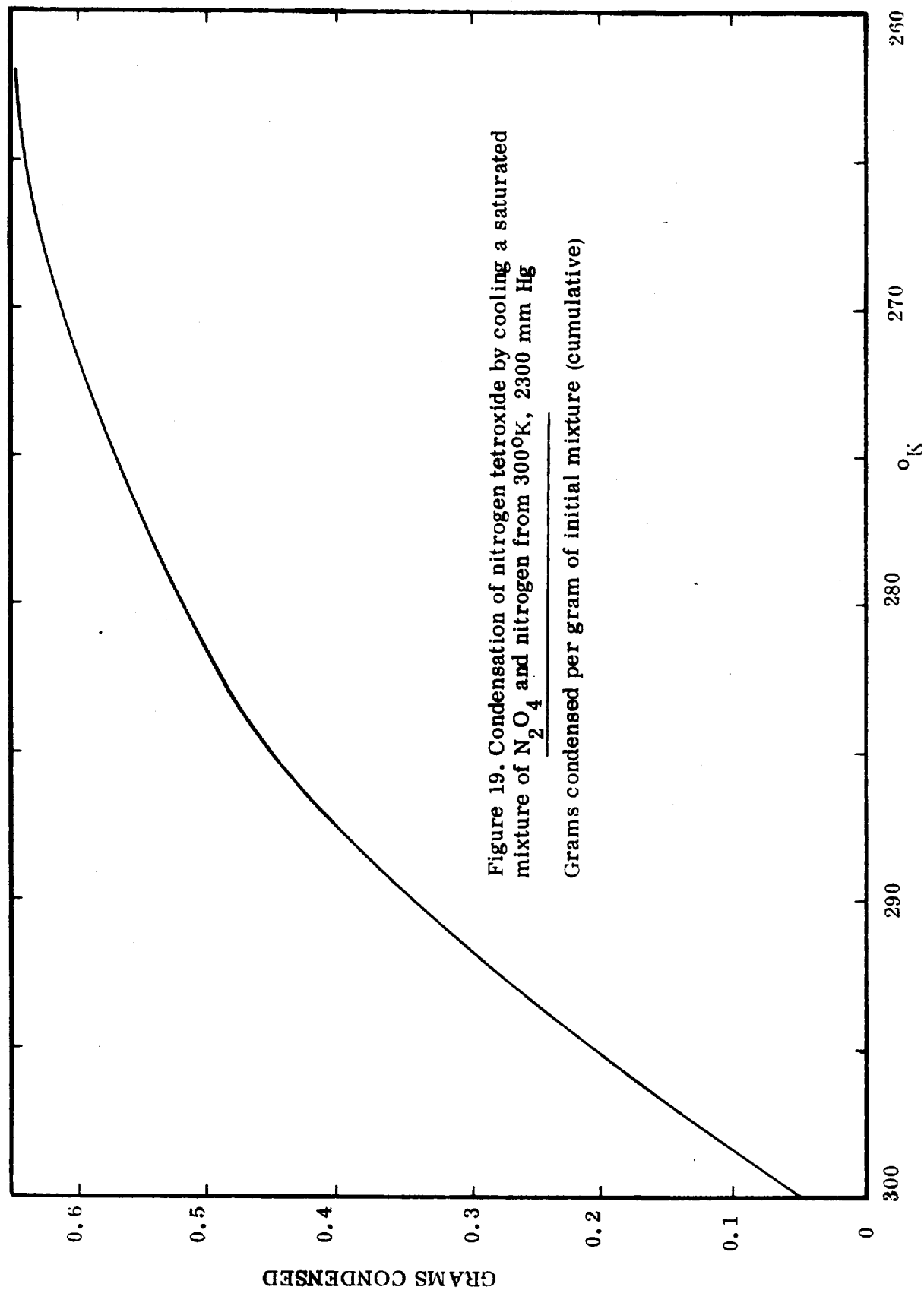
p being the pressure in atmospheres. In terms of α , the mole fractions of N_2O_4 and NO_2 are $(1-\alpha)/(1+\alpha)$ and $2\alpha/(1+\alpha)$, respectively, and the molecular weight of the equilibrium mixture is

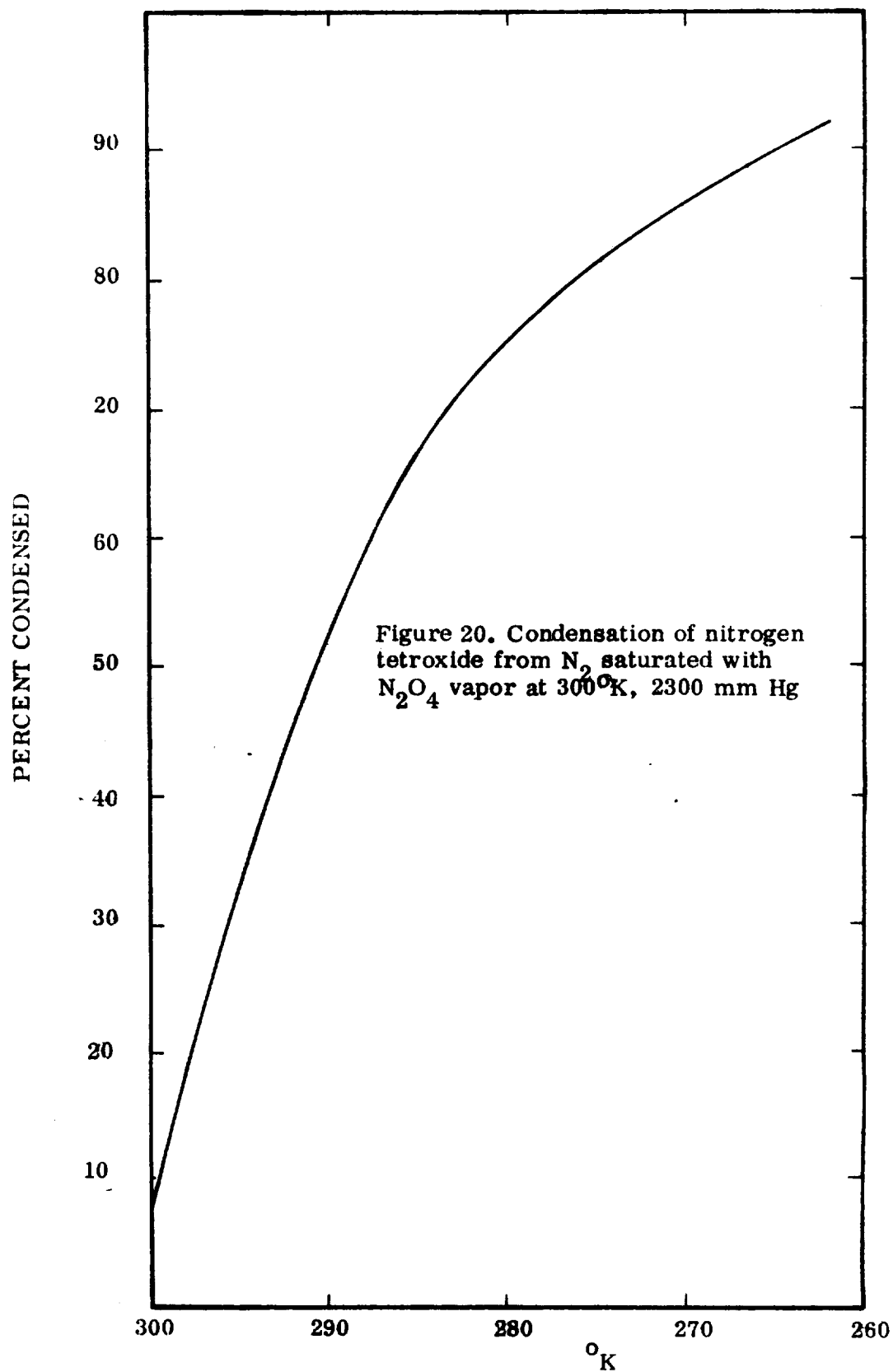
$$M = (46.008) + (1-\alpha) (92.016) .$$

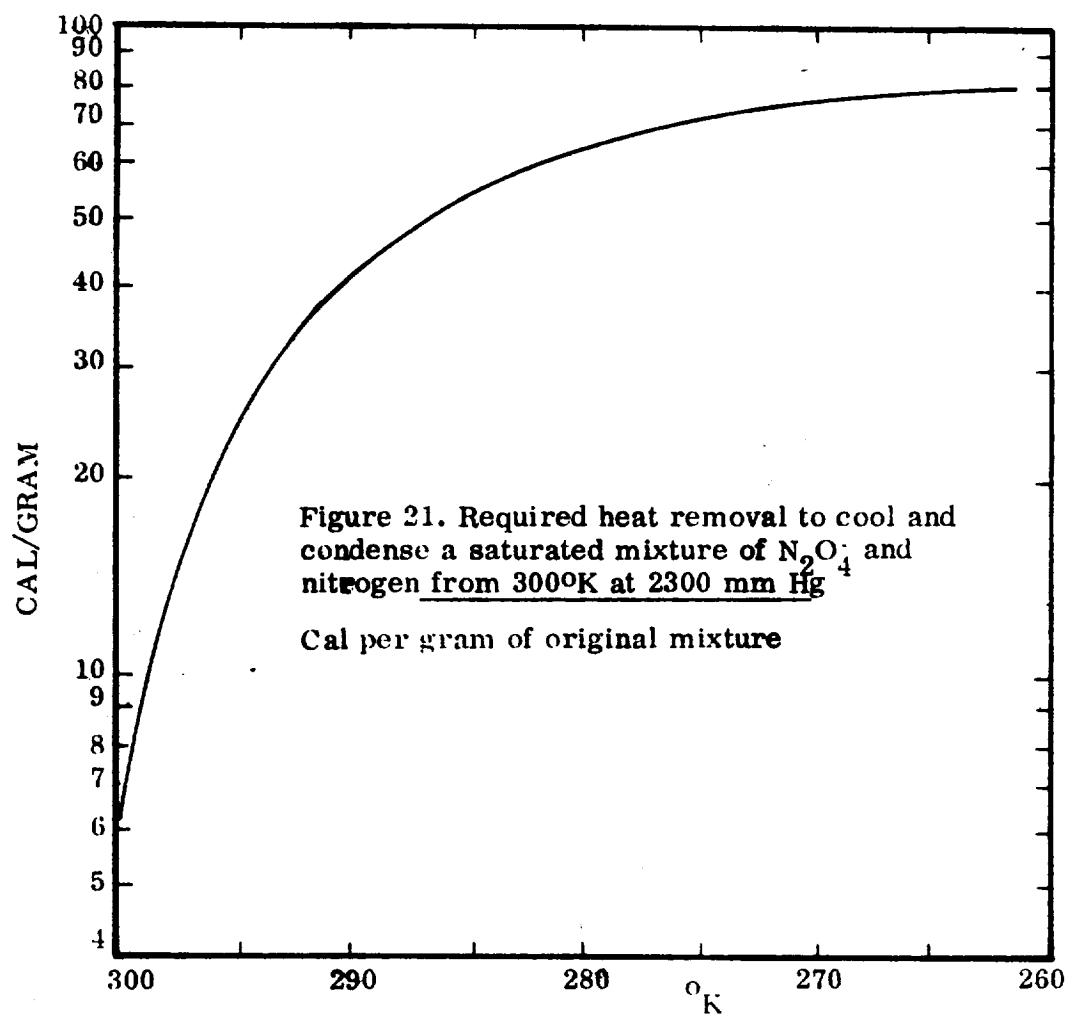
The results for α are presented in Appendix A; they were found to agree closely with other published data points.

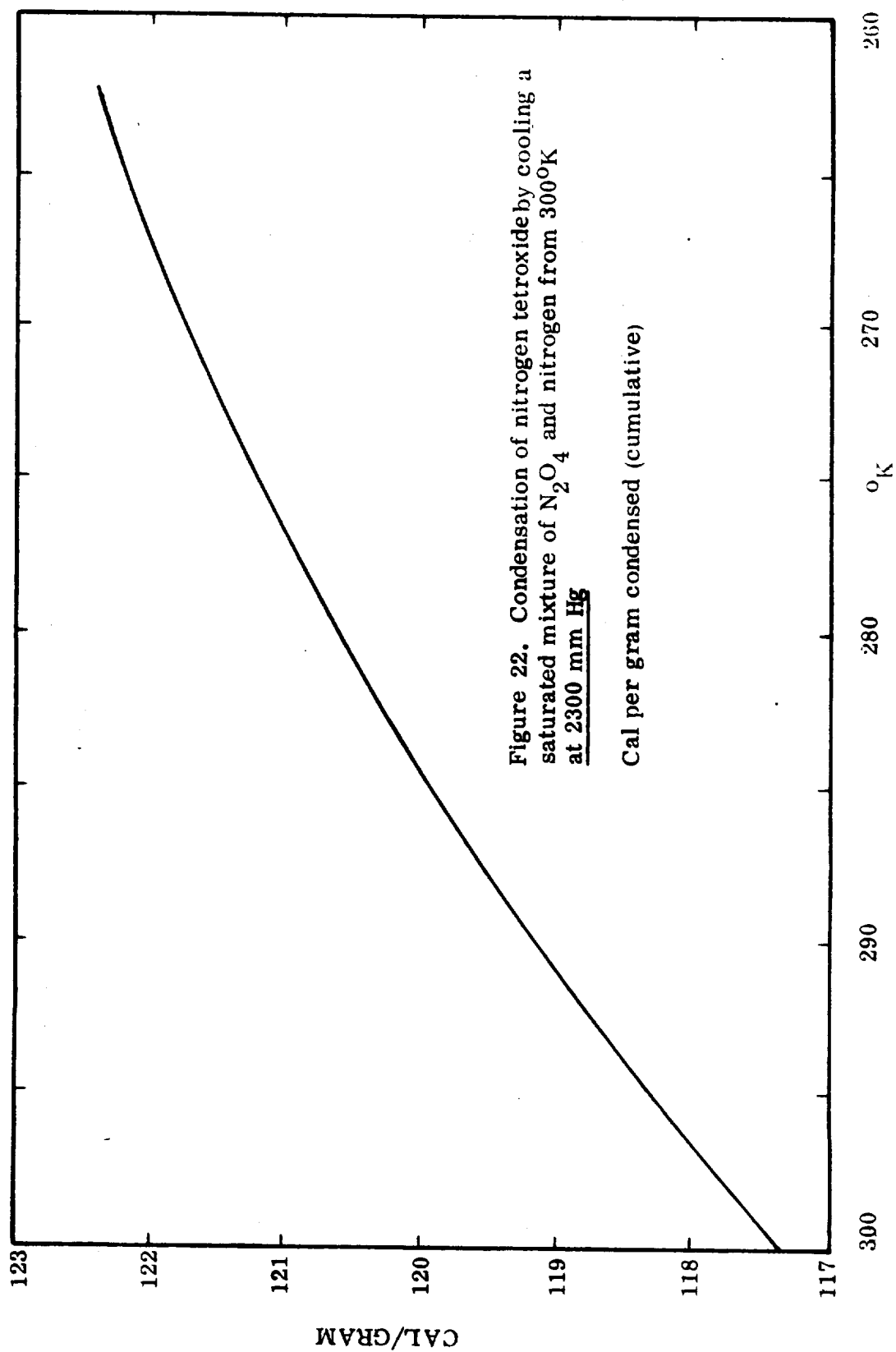
The vent gas was assumed to be nitrogen, saturated with $\text{N}_2\text{O}_4 - \text{NO}_2$, as in the hydrazine cases. The results are presented in Figures 19 through 23, which generally follow the same format as the corresponding Figures 14 through 18 and can be compared with those curves. The results are even more favorable than the hydrazine results.

¹⁰Yaws, C. L. and J. R. Hopper, "Oxides of Nitrogen: N_2O , NO , NO_2 ." Chemical Engineering, August 19, 1974.









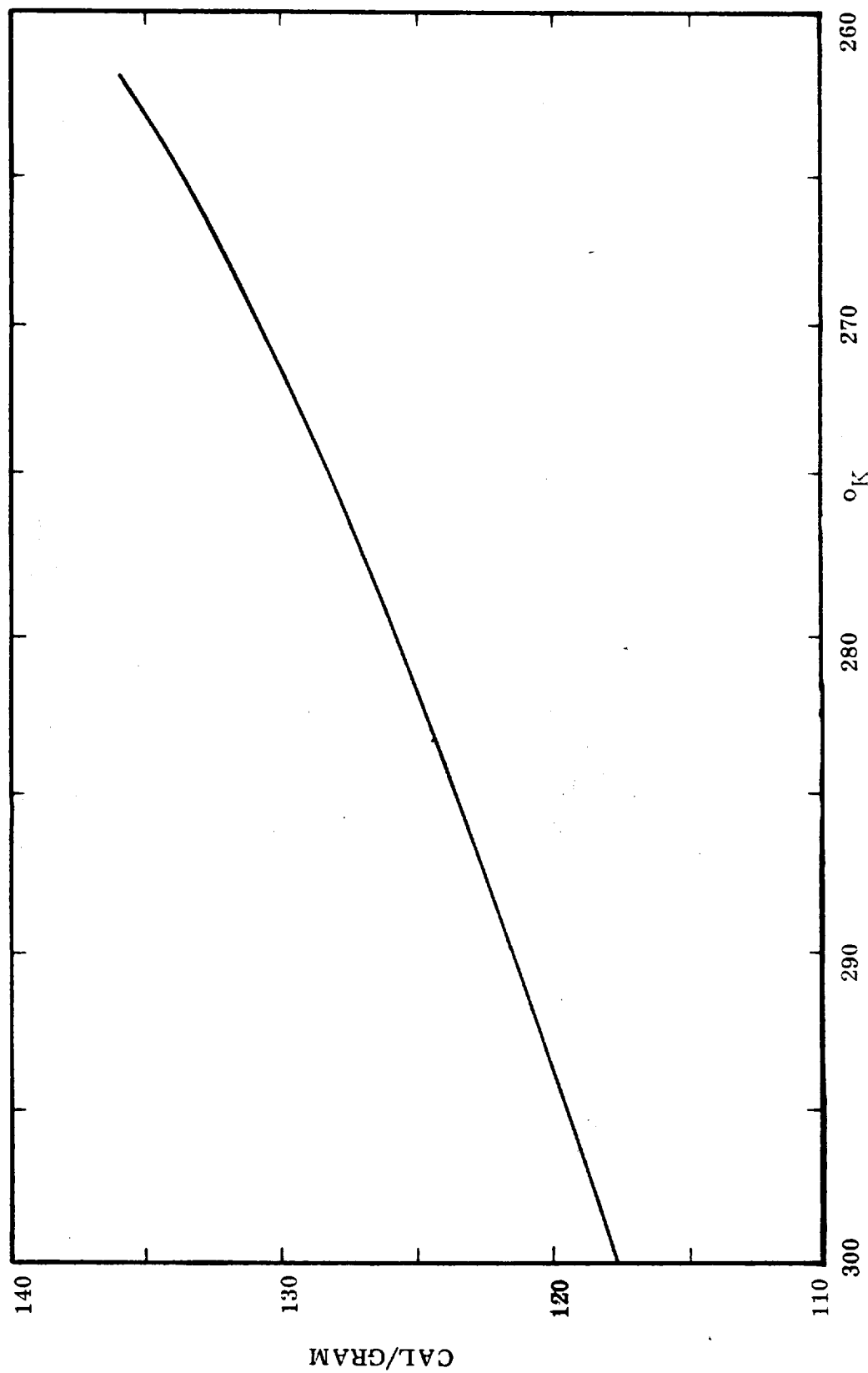
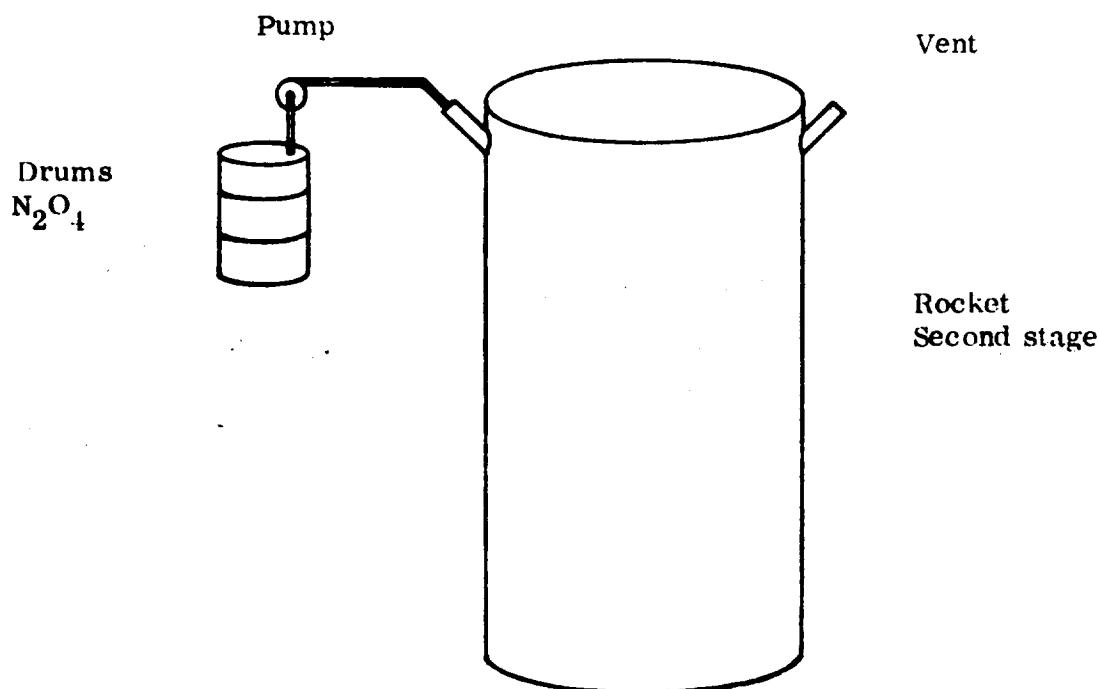


Figure 23. Condensation of nitrogen tetroxide by cooling a saturated mixture of N_2O_4 and nitrogen from $300^{\circ}K$ at 2300 mm Hg: Cal per gram condensed (incremental)

B. CONDENSATION OF N_2O_4 - NO_2 VAPORS

One of the most critical hypergol disposal problems is the effective disposal of N_2O_4 - NO_2 vapors vented during vehicle loading operations. It is estimated that 8000 gallons of N_2O_4 will be loaded onto the shuttle vehicle for each launch. A total of 480 gallons or slightly less than 5% is expected to be vented during the loading operation. The loading operation can be crudely visualized as shown in the sketch below, with vaporized N_2O_4 - NO_2 exiting straight out of the vent.

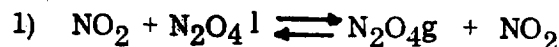
Venting of this amount of this highly toxic and noxious material is clearly not permissible.



A possible method of minimizing the amount of N_2O_4 - NO_2 released to the atmosphere would involve recondensation of vaporized N_2O_4 - NO_2 to the liquid form. This condensed material can then be either disposed of at a later time under more favorable conditions or reused as a hypergol.

As a prerequisite to consideration of recondensation as a disposal alternative, some fundamentals of the N_2O_4 - NO_2 system must be clearly understood.

Liquid N_2O_4 contains dissolved normally gaseous NO_2 , and gaseous N_2O_4 is in equilibrium with gaseous NO_2 as represented in the following equations



Thus it is seen that effective recondensation depends on a significant concentration of N_2O_4 existing in the gaseous state which in turn is favored by a positive free energy value and dissociation constant less than one.

The dissociation constant (K_p) in the gas phase is equal to the partial pressure (p) of NO_2 squared, divided by the partial pressure of N_2O_4 .

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} \quad (1)$$

If the term α represents the degree of dissociation of gaseous N_2O_4 as NO_2 , then $1-\alpha$ represents the number of moles of undissociated gaseous N_2O_4 and 2α the number of moles of NO_2 . Therefore $(1-\alpha) + 2\alpha$ or $1+\alpha$ is proportional to the total number of moles involved. If the total pressure is represented as P, the partial pressures involved are

$$P_{\text{N}_2\text{O}_4} = \frac{1-\alpha}{1+\alpha} P$$

$$P_{\text{NO}_2} = \frac{2\alpha}{1+\alpha} P$$

The dissociation constant K_p can therefore be given as

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha} P \right)^2}{\frac{1-\alpha}{1+\alpha} P} = \frac{4\alpha^2}{1-\alpha^2} P$$

At 25°C and P equal to one atmosphere, N_2O_4 has been found by vapor density measurements to be 18.46% dissociated ($\alpha = 0.1846$, see Table XXIV) giving $K_p = 0.141$.

TABLE XXIV

Equilibrium composition of $\text{N}_2\text{O}_4 - \text{NO}_2$, in terms of degree of dissociation of N_2O_4 (α)

Temperature °C	α 1 atm.	α 2 atm.	α 3 atm.
15	0.122	0.087	0.071
25	0.185	0.132	0.108
35	0.270	0.195	0.159
45	0.378		
55	0.502		
65	0.628		
75	0.741		

The standard free energy change can be calculated from the equation

$$\Delta F^0 = RT \ln K_p$$

where R = the gas constant, 1.987 cal/mole - °K
T = temperature in degrees Kelvin

giving $\Delta F^0 = +1161$ calories/mole.

These calculations show that at 25°C and one atmosphere N_2O_4 formation is favored in the gaseous state.

The heat of vaporization of N_2O_4 is 9.110 kcal./mole. This value is considerably higher than that calculated theoretically using Trouton's rule which simply states that the heat of vaporization, divided by the boiling point in degrees Kelvin, approximates 21

$$\frac{\Delta H_{\text{vap}}}{T} \approx 21$$

The boiling point of N_2O_4 is 21°C or 294°K. Thus theoretically, the heat of vaporization should be 6.174 kcal./mole. This large difference can be explained by the large dipole moment of NO_2 and N_2O_4 .

These data, and the results of the analysis of Section A all show that recondensation of N_2O_4 should be more practicable than one would intuitively expect merely considering the low boiling point and the readily observed dissociation into NO_2 . The following laboratory studies were therefore initiated in order to construct a model of a possible recondensation system.

A 500 ml. r.b. flask containing 50 ml. of N_2O_4 was connected to the top end of a conventional reflux condenser. The condenser was cooled with cooling water at various temperatures produced in a portable bath and circulator containing a refrigeration unit and a small water pump. The bottom end of the condenser was equipped with a receiver flask and a side arm which led to a sparger and which in turn was inserted into a small beaker of water (see Fig. 24). The circulating submersible pump used to circulate the cooling water was 1/150 horsepower. The pump circulated the water at a rate of 10 liters per hour.

The N_2O_4 was heated to 35°C and the vapors condensed in the receiver flask. The cooling water temperatures, the percent of N_2O_4 recovered and the time required for recondensation are listed in Table XXV.

TABLE XXV
Recondensation of N_2O_4

Cooling Water Temperature $^\circ\text{C}$	% Recovery of N_2O_4	Recondensation Time
-2.5	97%	10 mins.
0	88%	10 mins.
+5	80%	20 mins.

From these experiments, it seems that recondensation of vented N_2O_4 - NO_2 is very efficient using low temperature cooling water and may indeed be the method of choice for the disposal of vented N_2O_4 produced during the hypergol loading operation.

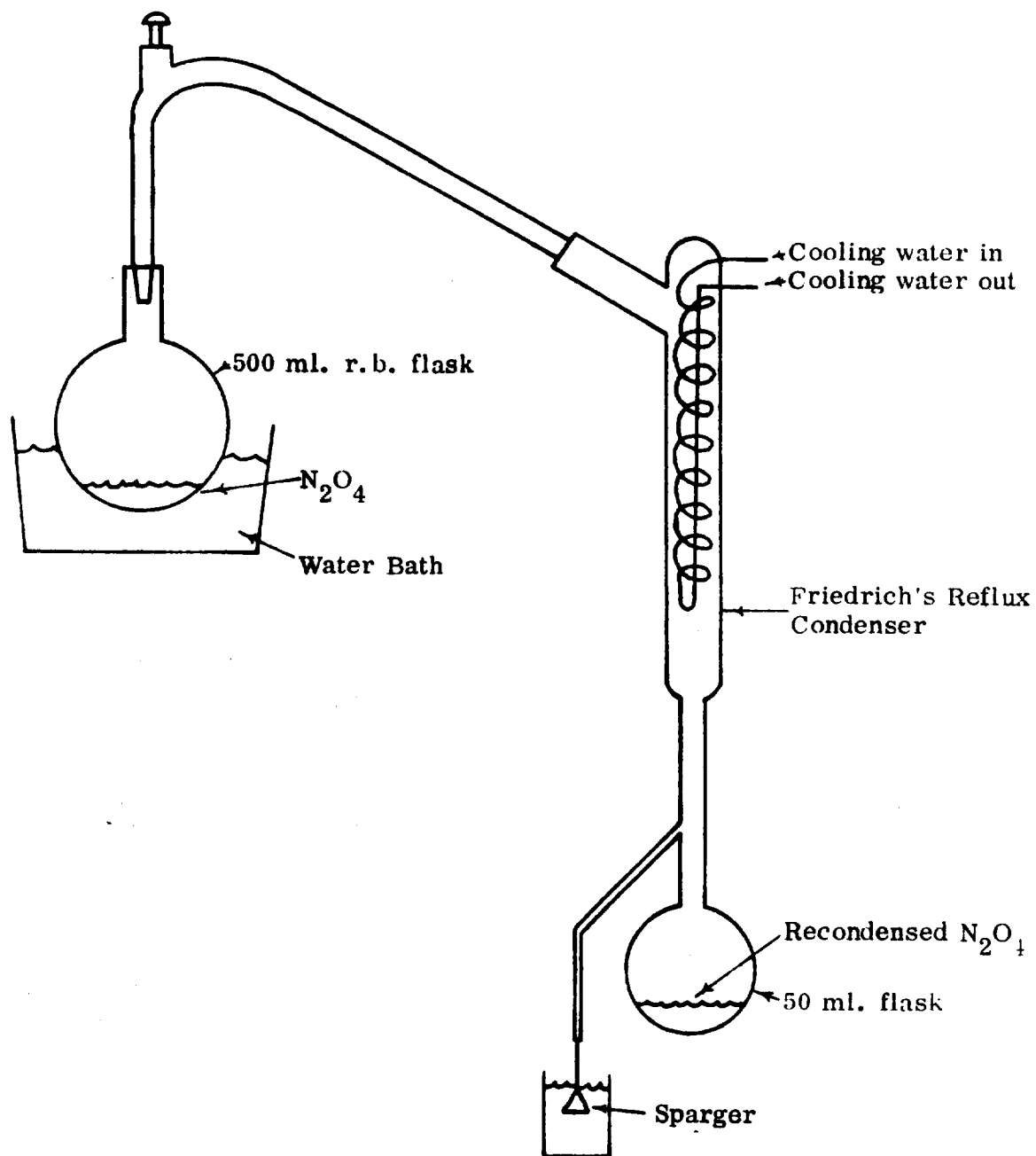


Figure 24. Experimental apparatus for recondensation of N_2O_4 .

C. DISTILLATION AND STEAM SCRUBBING OF MONOMETHYL HYDRAZINE

In order to create an experimental model, however imperfect, of the possible recondensation and scrubbing of vented monomethyl hydrazine (MMH) during the Shuttle hypergol loading operation, the following experiments were conducted.

A simple distillation of MMH was performed using an air-cooled condenser the dimensions of which are shown in Fig. 25. The room temperature at this time was 23°C. Starting with 25 ml. of MMH a total of 22.5 ml. or 90% was recovered in 15 minutes. The ratio of the volume of air in the system to the volume of MMH was 11:1.

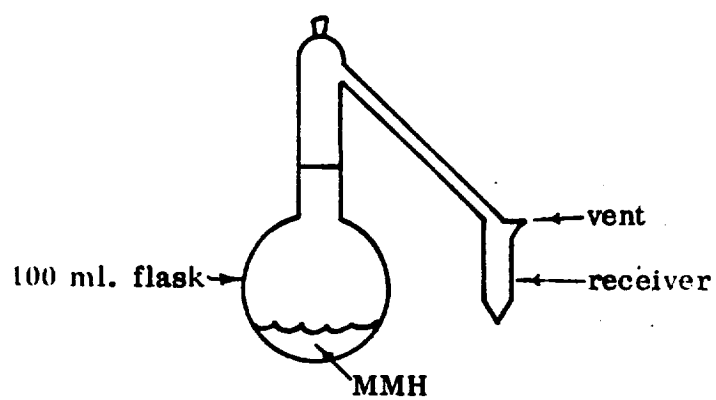
A second series of experiments was run similar to the above except that a water cooled condenser and 5°C cooling water was used. The data in Table XXVI denote the initial starting volumes of MMH, the ratio of the volume of air in the system to the initial starting volume of MMH, the volume of MMH recovered, and the percentage recovery (see Fig. 26).

TABLE XXVI

MMH Initial Volume (ml.)	Condensation of MMH		Vol. Recovered (ml.) MMH	% Recovered
	Vol. Air	MMH Initial Volume		
5	68.4		4.8	96
10	33.7		9.8	98
20	16.4		19.5	98
30	10.6		29.0	97
40	7.7		39.0	98

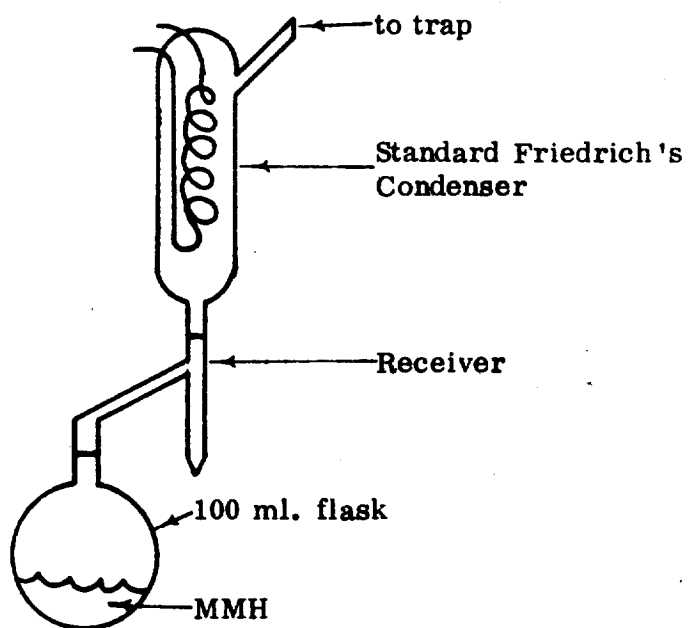
A third series of experiments was conducted in which an attempt was made to combine the model recondensation system with a model scrubbing system. Since a source of a fine spray of water was unavailable, steam was used as the scrubbing agent. The apparatus was set up as shown in Fig. 27. Initially, 10°C cooling water was used and a starting volume of 25 ml. of MMH with a volume of air to volume of MMH ratio of 95.6. Five hundred ml. of water was converted to the steam which was used for scrubbing. Also, 24.0 ml. of MMH (96%) was recovered in the receiver flask as assayed using the DAB method*.

* See Appendix B



Total vol. of air outside of flask = 203 ml.

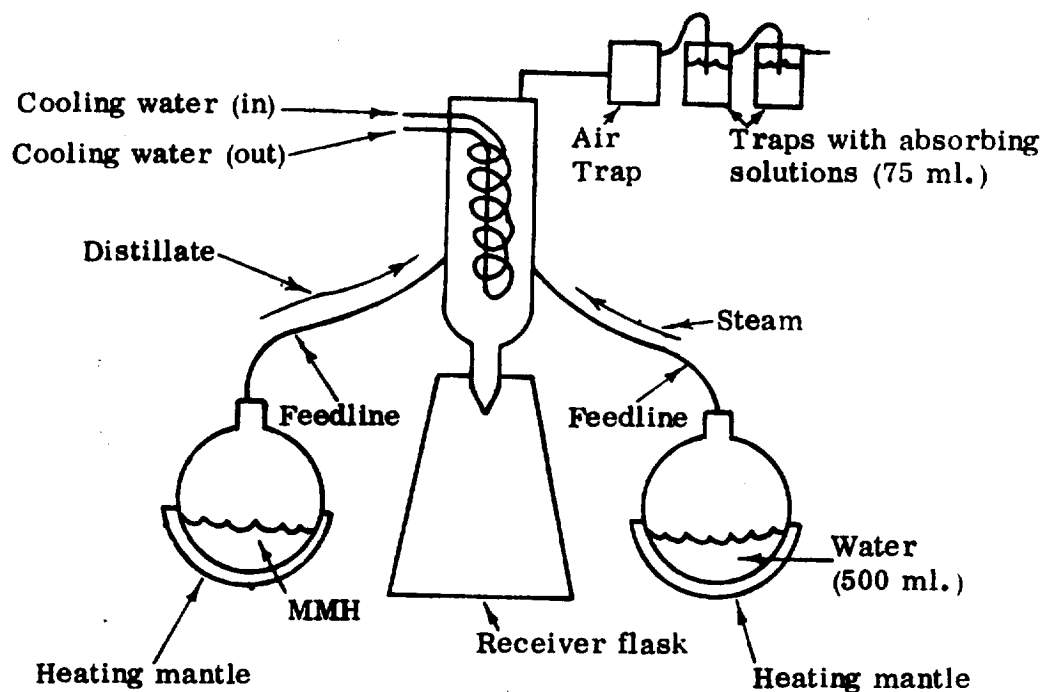
Figure 25. Experimental apparatus for distillation of MMH and air cooled condensation.



Air volume outside of distillation flask = 247 ml.
 Cooling coil volume = 190 ml.

Cooling water flows at a rate of 30 liters/hr. at 5°C.

Figure 26. Experimental apparatus for distillation of MMH and water cooled condensation.



Dimensions

1. Receiver (vol.)	1100 ml.
2. Steam Generator flask (vol.)	1000 ml.
3. Distillation flask (vol.)	100 ml.
4. Cooling coil (vol.)	38 ml.
5. Condenser (vol.)	400 ml.
6. Feed line (vol.)	8 ml.
7. Feed lines (length)	50 cm.
8. Diameter cooling coil	0.5 cm.
9. Traps (vol.)	150 ml. (ea.)
10. Length of cooling coils	25 cm.
11. Width of cooling coils	3 cm.
12. Number of coils	15

Figure 27. Model recondensation steam scrubbing disposal system

A fourth series of experiments was performed analagous to the above except that varying volumes of MMH were distilled and the cooling water temperature was 5°C. Steam was generated for varying amounts of time depending on the amount of MMH to be distilled, but steam was always generated starting ten minutes before distillation and ending ten minutes after completion of distillation. The data are shown in Table XXVII.

MMH was not found in the traps and, therefore, the most likely explanation for the poorer recoveries at the lower volumes is decomposition or oxidation in the distillation flask.

TABLE XXVII

Distillation and Steam Scrubbing of MMH				
MMH Initial Volume (ml.)	Vol. Air MMH Initial Vol.	Vol. Recovered MMH (ml.)	%Recovered	Vol. (ml.) Steam used (as water)
50	46.8	49.1	98.2	375
40	58.8	40.1	100.1	445
30	78.7	29.9	99.7	425
20	118.6	19.4	97.0	245
10	238.1	9.2	92.0	170
5	477.2	4.0	80.0	165

The results of the experiments would seem to indicate that a recondensation scrubbing disposal system for MMH is feasible. Unfavorable conditions which were present in these experiments such as distillation under one atmosphere of air would not be present under actual operating conditions where loading of MMH is conducted under nitrogen pressure of one to three atmospheres. It is possible to envision an apparatus attached to the vent port of the rocket which would recondense the majority of the fuel and scrub the remainder, thus allowing very little if any escape of fuel vapor to the atmosphere (Fig. 28).

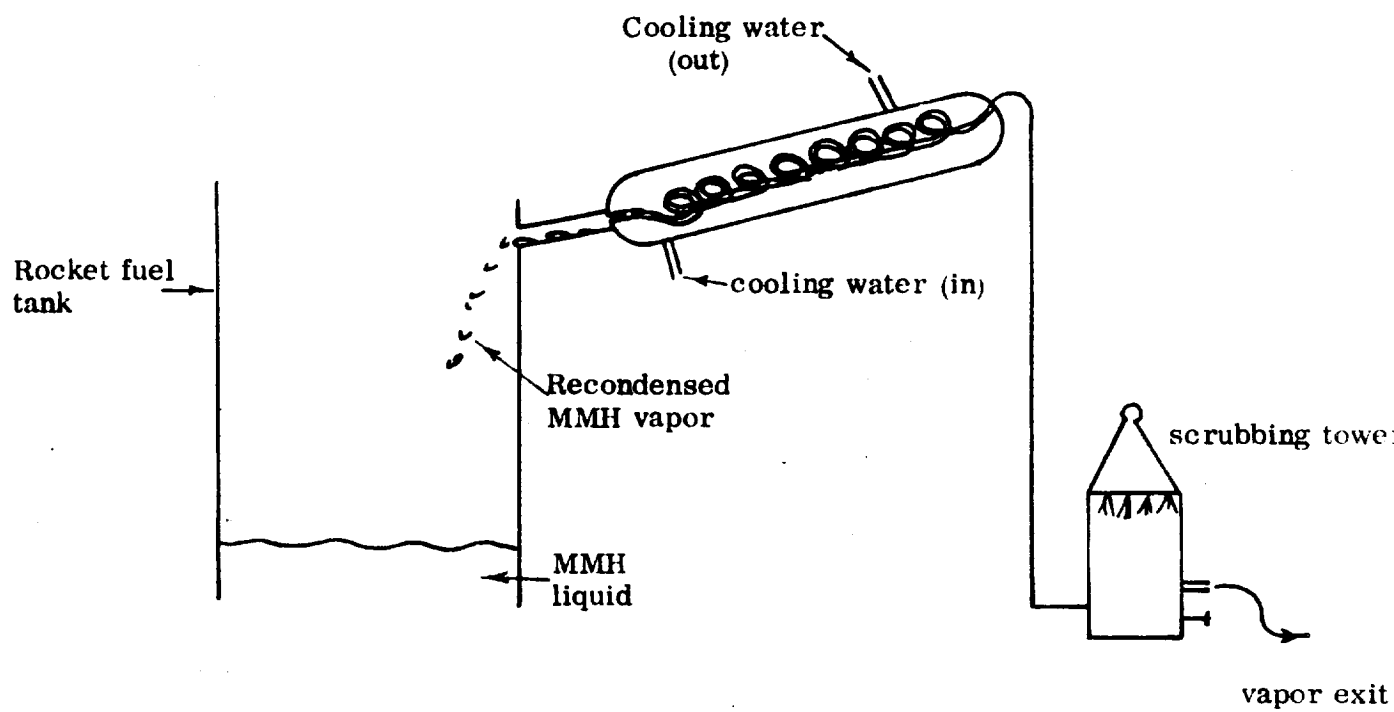


Figure 28. Proposed recondensation scrubbing disposal system

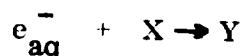
III. DESTRUCTION OF N_2H_4 , MMH OR N_2O_4 BY GAMMA IRRADIATION

OBJECTIVE: To Determine the Effect of Gamma Radiation from Cobalt - 60 on the Decomposition of Waste Hypergols.

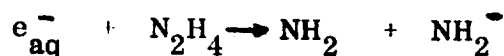
1. Background

In the irradiation of water solutions, destructive oxidation of organic/inorganic molecules takes place by direct energy absorption which ruptures the bonds in the molecules, followed by O_2 combining with the free radicals formed. Much of the oxidation occurs due to the indirect attack by the hydroxyl radical (OH^\cdot) resulting from radiolysis of water as well as from the hydrated electron (e_{aq}^-). The hydrated electron is a highly reactive negative ion that appears to be a more powerful reducing agent than the H atom. The e_{aq}^- particle is considered to be the dominant species in irradiated water and is utilized to explain many of the radiolytic processes.¹

The nature of the reaction of the hydrated electron is given by:



For example, in the case of N_2H_4



There are several empiric values used to assess the efficiency of a radiation initiated reaction. One of these is called the G value and another is the absorbed radiation dose (Rads) required to achieve the destruction of a species or combination of organic/inorganic species.

The G value is defined as the number of molecules of chemical compounds which are formed, changed, or disappear; or the number of oxidation reactions which occur as a result of the absorption of 100 electron volts of energy.

A Rad is approximately equal to the absorbed dose delivered to material exposed to one roentgen of medium voltage X-radiation.

$$1\text{Rad} = 100 \text{ erg/gram}$$

¹Hart, E. J., Record Chem. Prog., Vol. 28, p. 25 (1967).

2. The Cobalt-60 Facility at F. I. T.

The Cobalt-60 facility at Florida Institute of Technology is operated by the University Center for Pollution Research (UCPR). The gamma rays from the 27,000 Curie source are of the electromagnetic type which are more suitable for treatment of liquids because of the lack of residual radioactivity in the irradiated material.

3. Experimental Procedure

The diluted samples of MMH, N_2H_4 and N_2O_4 were poured into 4 oz. glass bottles, capped and exposed to the Co^{60} gamma source for the required period for dosages of 10^4 , 10^5 or 10^6 rads. The controls and the exposed samples were analyzed for residual concentrations of undecomposed hypergols. The results appear in Table V.

4. Methods of Analysis

The analyses were performed according to methods listed in the 13th edition of STANDARD METHODS FOR THE EXAMINATION OF WATER AND WASTEWATER, published by A. P. H. A. For hydrazines, the p-DAB procedure was followed (see Appendix C). A Bausch & Lomb Spectronic - 20 spectrophotometer was utilized in determining concentrations of the hydrazines or nitrate.

5. Results

As shown in Table XXVIII, irradiation of aqueous solutions of MMH, N_2H_4 or N_2O_4 results in partial destruction of the hypergols.

In Test 1, N_2H_4 concentration was reduced by more than 8% in approximately 1 1/4 hours from the 75,000 ppm level (7.5%).

In Tests 2, 4 and 5, N_2O_4 concentration was reduced approximately 12-14% in 1 1/4 hours from various concentration levels.

In Tests 3 and 6 the MMH concentration was reduced approximately 17% in 7 1/2 minutes and approximately 26% in 1 1/4 hours.

6. Discussion

The hydrazines decompose to yield N_2 , H_2 , and possibly some CO_2 with MMH, creating a slight pressure in the screw-capped bottle. (This reaction is essentially irreversible.) These products are environmentally safe for disposal. The gaseous pressure problem can be relieved by having an open system.

TABLE XXVIII

Gamma Radiation Experimental Results

Test	Dose in KR	Time Irradiated	N ₂ H ₄ ppm	MMH ppm	N ₂ O ₄ ppm (as NO ₃)	% Reduction from Control
1	0(Control) 1,000	0 74.5 min.	74,500 68,000			8.72
2	0(Control) 1,000	0 74.5 min.			18,480 16,280	11.9
3	0 10 ⁴ 10 ⁵	45 sec. 7.5 min.		12.1 10.7 9.9		11.5 18.2
4	0 10 ⁴ 10 ⁵ 10 ⁶	45 sec. 7.5 min. 74.5 min.			1925 1870 1760 1650	2.9 8.6 14.3
5	0 10 ⁴ 10 ⁵ 10 ⁶	0 45 sec. 7.5 min. 74.5 min.			50,600 48,400 44,000	4.3 13
			Bottle Leaked			
6	0 10 ⁴ 10 ⁵ 10 ⁶	0 45 sec. 7.5 min. 74.5 min.		52,500 50,000 43,400 38,800		4.75 17.3 26.1

N_2O_4 decomposes to yield NO_X and N_2 , thus creating a secondary disposal problem. In a closed system, as in the screw-capped bottle, the evolved NO_X will collect in the gaseous phase and set up an equilibrium with the liquid. It may be assumed that complete destruction by continued gamma radiation will not be easily achieved due to this equilibrium. Sufficient radiation of NO_X to form N_2 may require an uneconomically long period of time.

From an environmental viewpoint, radiological destruction of the hydrazines offers certain advantages. The formation of elemental gases and water eliminates the toxicity problem from waste effluent being discharged into streams. No additives, as neutralizing or oxidizing agents (NaOH, hypochlorites, etc.) are necessary, thereby eliminating the need for chemicals.

On the other hand, it was noticed that under the test conditions (screw-capped bottle) there was a build up of pressure in the bottle due to gas generation. In addition to the expected N_2 gas an odor of NO and the brown fumes of NO_2 were noticed on uncapping the bottle. These NO_X present a secondary disposal problem.

Past experience at Palmdale* indicated direct operating costs of under \$1.00 per 1,000 gallons of waste water treated, including a filtration system. The initial construction cost of a radiation facility is approximately twice the cost of a conventional facility. Operating costs for a hypergol treatment facility may be anticipated to be higher due to the larger dosages required for chemical compound destruction, with concomitant increased exposure time and pump recirculation costs. Our preliminary estimate is that operating costs would be less than 5 times the above cost - less than \$5 per 1000 gallons treated.

The cost of chemicals alone used in treating 1000 gallons of 1% MMH solution (80 lbs. contained MMH) would amount to \$160.00 if H_2O_2 is the neutralizing agent. (See Table XIV, page 92).

In the final analysis, the overall costs of both methods must be evaluated in order to obtain comparative figures.

Figure 29 shows a plot of dosage vs. MMH concentration. The G value, used for assessing the efficiency of a radiation reaction was not determined. A possible synergistic effect by bubbling O_2 or O_3 during irradiation was not explored due to time limitation. It is believed that destruction of MMH would be enhanced due to strong oxidizing conditions.

*This was a 16,000 curie Co^{60} facility treating approximately 10,000 gallons daily, located at Palmdale, Florida, for disinfection purposes.

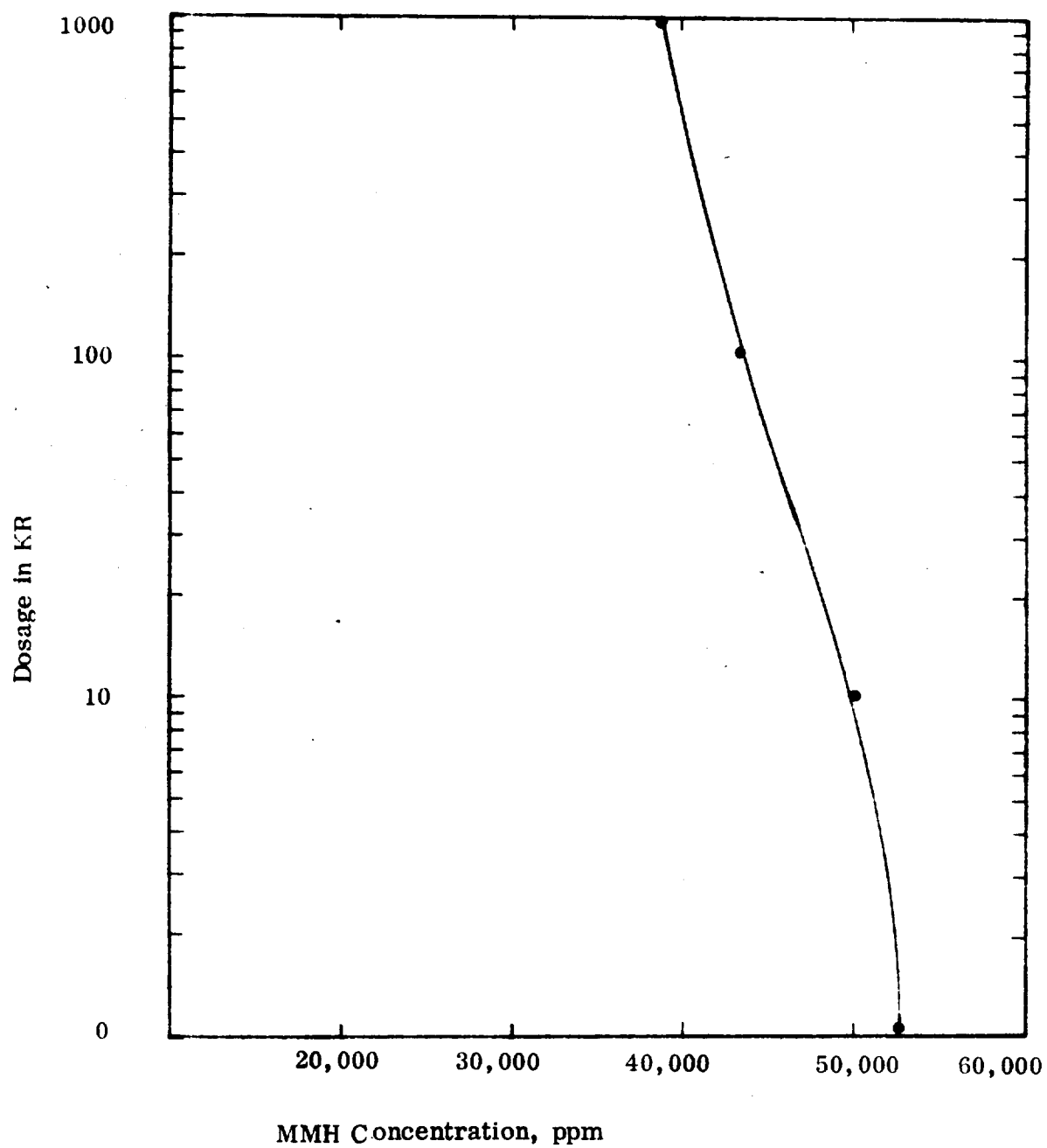


Figure 29. MMH decomposition by cobalt-60 irradiation after 74.5 minutes.

7. Conclusions

Results of this work indicate that the destruction of N_2H_4 , MMH or N_2O_4 by gamma radiation from Co^{60} is possible.

More decomposition occurred than was anticipated for hydrazine type compounds at the relatively small dosages used.

The radiation/destruction approach is worthy of continued effort if only to establish the lability of the 3 hypergols briefly looked at above.

The environmental aspect of radiological destruction of N_2H_4 and MMH looks favorable; N_2O_4 may present a gaseous disposal problem at high N_2O_4 concentrations.

On the basis of the preliminary work, it is recommended that further work be carried out to study the pertinent parameters involved in the gamma destruction method for disposal of hydrazines.

IV. CATALYTIC DECOMPOSITION

It is apparent from chemical considerations that waste and contaminated hypergolic propellants might be effectively eliminated by catalytic decomposition. This section of the report discusses some aspects of the technique and the possibilities for application. The use of catalysts also entered into the experiments described in Section III. A of the "Application Studies" portion of this report.

Reactions occurring entirely within a single phase are referred to as homogeneous, while those occurring at an interface are heterogeneous. Experimentally one finds that the activation energy for the latter is lower; the magnitude of the differential is a complex function of several thermodynamic parameters. Catalysts are simply a relatively stable interface introduced into the system to supply a favorable reaction site.

Catalysts are particularly important for exothermic reactions. Although the equilibrium constant is such that the reaction should proceed at, say, room temperature, the rate may be prohibitively slow. From the empirical Arrhenius equation

$$\text{Rate} = A \exp\left(\frac{-\Delta E_a}{RT}\right),$$

where ΔE_a is the activation energy, one would expect a satisfactory rate to obtain by a sufficient increase in temperature. However, according to Le Chatelier's principle, whenever an equilibrium system is perturbed the system will attempt to readjust in such a way as to oppose the applied change. So when the temperature is increased the equilibrium shifts in the direction which causes an absorption of heat, thereby requiring an additional increment of heat to raise the temperature. Stated mathematically the temperature dependence of the equilibrium constant is

$$\frac{\partial \ln K}{\partial (1/T)} = \frac{-\Delta H}{R}$$

Catalysts are the means by which the reaction can be carried out at temperatures where the equilibrium constant is favorable.

The use of a catalyst for decomposing hydrogen peroxide was briefly mentioned in the portion of this report on "Evaluation of Current Disposal Methods." To further investigate the possibilities of this technique,

letters were sent to organizations believed to be active or at least knowledgeable in the field: Engelhard Industries, Inc., Matthey Bishop, Inc., and International Nickel Co., Inc. Matthey Bishop has not replied and Mr. R. B. Teel of International Nickel provided five more leads: Harshaw Chemical Co., Chemetron Corp., Monsanto Chemical Co., W. R. Grace & Co., and International Copper Research Association, Inc. Of these, only Chemetron has failed to respond; neither INCRA nor Monsanto could offer assistance.

W. R. Grace & Co., Baltimore, responded with:

"Hydrogen peroxide could be decomposed over a manganese catalyst such as our Grade 908.

"The hydrazines would also be relatively easy to decompose using Raney nickel catalyst.

"The N_2O_4 and HNO_3 pose the most difficulty in decomposition. A catalyst containing platinum or palladium used in a reducing atmosphere of hydrogen or carbon monoxide would probably do the job. Unfortunately we do not have such a catalyst available."

Decomposition generally requires 3-5 percent of catalyst on a weight basis. In lots of 100 to 1000 pounds the Mn908 is \$3.85 per lb (f.o.b. Baltimore), and the Raney Ni 28 is \$4.05 per lb. (f.o.b. So. Pittsburgh, Tenn.).

The Harshaw Chemical Co., Cleveland, supplied information on two nickel catalysts developed by the Jet Propulsion Laboratory for the decomposition of hydrazine. Indications are that their use is limited to the controlled decomposition of monopropellant hydrazine used in space probes. The price quoted for the two nickel catalysts in 100 lb lots was approximately \$5 per pound.

If we assume that 4 weight percent catalyst is needed for decomposition, the disposal of 8000 gallons of N_2H_4 (3×10^4 kg) would require 1.2×10^3 kg of catalyst. At \$11 per kg (\$5 per lb) this is \$13,200 worth of catalyst, or \$1.65 per gallon of fuel disposed. The catalyst probably can be regenerated to reduce cost, perhaps substantially, but this is an unknown at present. The poisoning effects of impurities in the waste fuels would have to be investigated.

The Systems Department of Engelhard Industries responded with little conclusive information. They have no confirmed processes directly applicable to

the propellants of interest but suggest that the disposal of N_2O_4 by dilution with air and catalytic decomposition analogous to nitric acid tail gas would be feasible. In a paper by several of their people¹ a system is described which they believe will decolorize the effluent and reduce the NO_2 level to approximately 200 ppm (Fig. 30).

The manufacture of nearly all nitric acid begins with the catalytic oxidation of ammonia to form NO , which reacts with residual oxygen to form NO_2 . This is absorbed in water forming HNO_3 and additional NO . For maximum power recovery the gases are heated by direct catalytic combustion of the NO_2 before entering the expander. If additional fuel is added the total nitrogen oxides are reduced to the 100 - 1000 ppm range.

The major problem in earlier systems was the reduction of catalyst activity or short catalyst life. Engelhard feels they have overcome these problems with a system employing a spherical palladium catalyst, fuel desulfurization, and process control features for temperature control, fuel/oxygen ratio and thermal protection of the catalyst.

Apparently the technology is available to solve the problems of catalytic decomposition of hydrogen peroxide, nitrogen tetroxide, and the hydrazines. The HF inhibited nitric acid poses difficulties; experience shows that halogens have a deleterious effect on catalyst life and activity.

Engelhard has offered to quote on a study to explore the economics, effectiveness, problems, potential catalyst poisons, etc.

One of Engelhard's products which may be worth investigating further is "CHLOROPAC", an electrolytic sodium hypochlorite generator. It is a modular system producing hypochlorite solution directly from ocean water, with a capacity in any desired range. In the section on Evaluation of Current Disposal Methods, peroxide was chosen over the hypochlorites for the neutralization of hydrazines; one of the bases of evaluation was cost. A device such as this may call for reevaluation.

Dr. Robert Ottinger, the author of the extensive TRW Report, has advised that the inexpensive catalyst mentioned in that report is molybdenum based.

¹Gillespie, G. R., A. A. Boyum and M. F. Collins, "Catalytic Purification of Nitric Acid Tail Gas: A New Approach." Presented at the AIChE Annual Meeting, San Francisco, December 2, 1971.

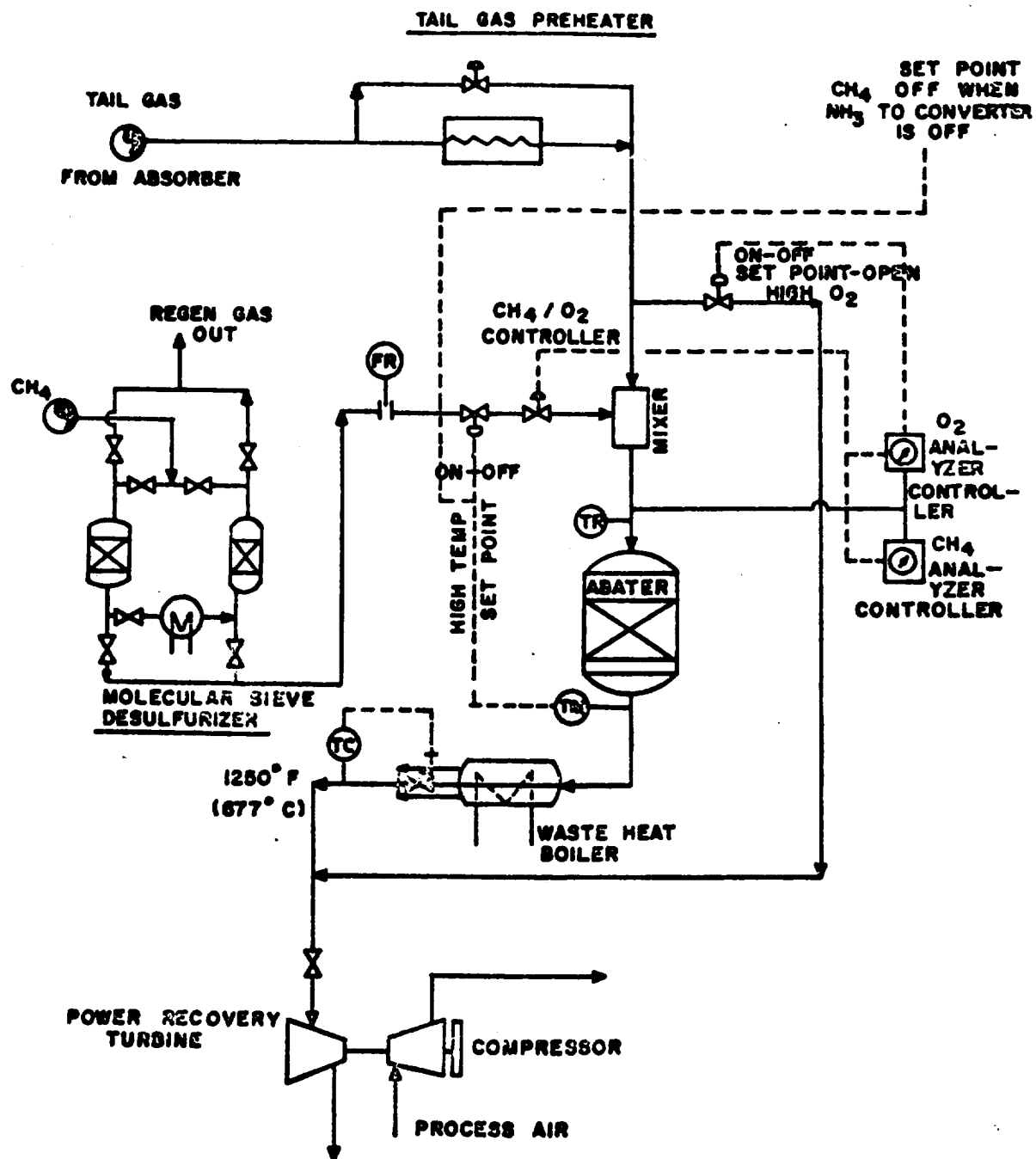


Figure 30. NO_x Abater System I, reproduced from Gillespie et. al.

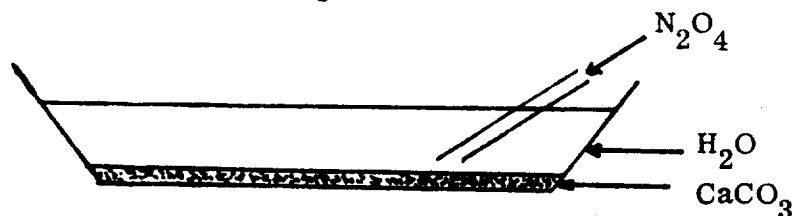
Further information on current development was promised, but has not yet been received.

It has been learned that one supplier's proprietary catalyst for N_2H_4 is a mixture of iron and iron oxide. If further study is decided upon, a series of experiments using rusty automobile body sections might be worthwhile.

V. CALCIUM CARBONATE AS A NEUTRALIZATION AGENT FOR N_2O_4

1. The Calcium Carbonate Disposal System

The disposal of large quantities of N_2O_4 presents numerous problems. Thermal reduction is possible but requires special equipment. Neutralization with a soluble base such as Na_2CO_3 , NaHCO_3 or NaOH results in exothermic reactions and the problem of disposal of excess neutralizing solution into biologically sensitive ocean, river or groundwater systems. A possible solution to these problems is a water insoluble neutralizing agent. The cheapest and most readily available is Calcium Carbonate (CaCO_3). A large pool could be dug and on the bottom could be layered CaCO_3 and water.



The N_2O_4 could be fed to the aqueous layer. In a matter of time, only that amount of CaCO_3 would be dissolved as was necessary to neutralize the N_2O_4 fed to the system. Thus, no high degree of exothermy would be necessary. After neutralization, the solution would be at or near neutrality (pH 7). The dissolved chemicals would be the minimum necessary to neutralize the oxidants, and thus disposal problems of the aqueous layer would be minimized.

To determine the feasibility and desirability of pools of this type, a series of laboratory experiments was conducted.

2. Experimental Results

A receiver vessel layered with CaCO_3 and water was prepared. To this solution was added N_2O_4 . The water temperature and pH were monitored and the time and dilution necessary to safely dispose of given quantities of N_2O_4 without seriously raising temperatures were determined.

The receiver contained two liters of tap water, and 250 gm. of finely powdered CaCO_3 was prepared. The CaCO_3 was layered on the bottom to a depth of 5mm. In a separate flask 25 ml. of N_2O_4 was placed. A 1/8" glass tube was inserted into a rubber stopper which was fitted to the flask. The other end of the glass tube was inserted into the receiver to a level just above the CaCO_3 (see Fig. 31). The flask containing the N_2O_4 was heated to 35°C with a water bath and N_2O_4 vapor and liquid proceeded into the receiver for 15 minutes .

The pH of the receiver solution dropped from 8.0 to 1.0 over this period of time while the temperature varied slightly from 21 to 22°C . The bubbles of $\text{NO}_2\text{-N}_2\text{O}_4$ were large, however, and a red cloud was observed over the receiver. When the time of addition of N_2O_4 was increased to 0.5 hr. the amount of red gas over the receiver was considerably diminished.

A second experiment (see Table XXIX) was conducted similar to the one described with an important exception. Limestone chips 0.75 inches in diameter were used in place of the finely powdered CaCO_3 . The other parameters and data were as follows:

Wt. of CaCO_3	400 g.
Vol. of H_2O	1.8 l
Vol. of N_2O_4 added	25 ml.
Time	20 minutes

TABLE XXIX
Addition of N_2O_4 to Water over CaCO_3 Chips

<u>Time mins.</u>	<u>pH</u>	<u>Receiver Temperature</u>	<u>Comment</u>
0	3.5	21°C	Contact of N_2O_4 vapor with water
10	1.0	21°C	
15	1.0	21°C	
20	1.0	21°C	Vigorous CO_2 evolution
24 hr.	4.0	19°C	End of CO_2 evolution

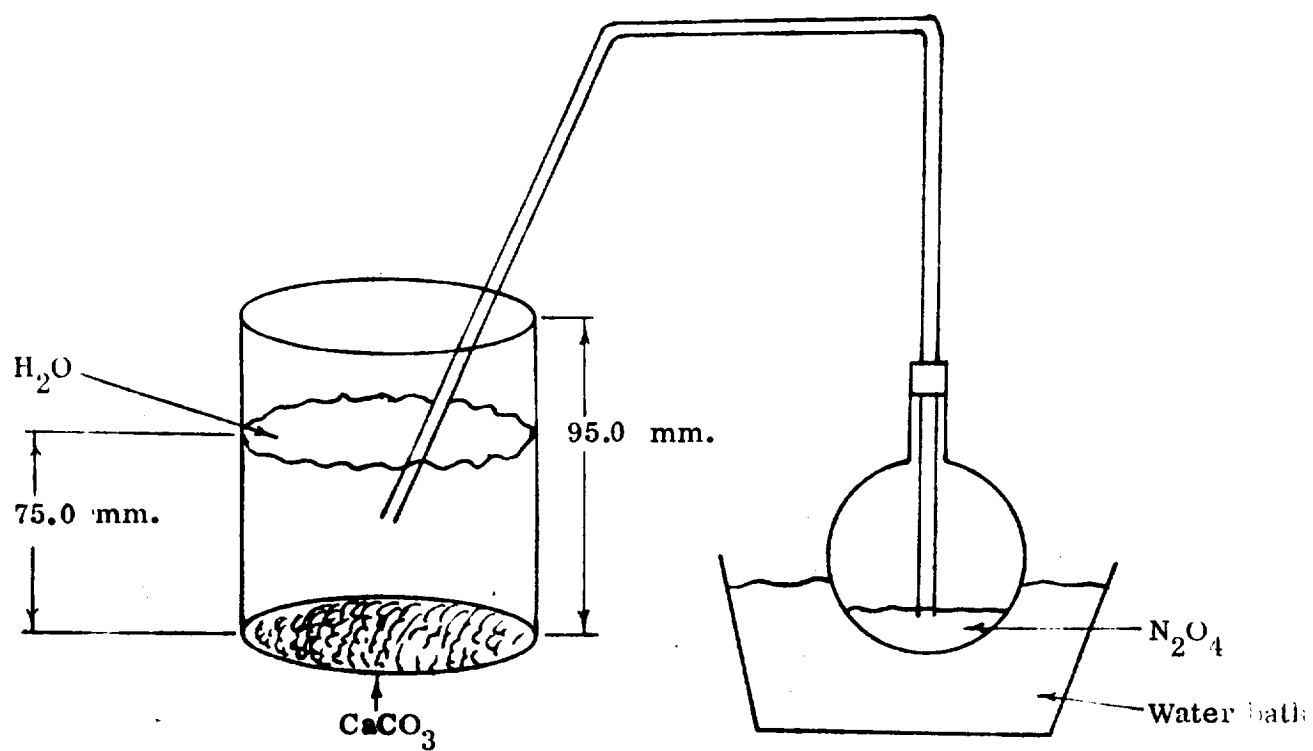


Figure 31. Addition of N_2O_4 to water over calcium carbonate.

Again, large bubbles of $\text{NO}_2\text{-N}_2\text{O}_4$ were observed and a small amount of red gas (NO_2) was observed over the receiver.

The data indicated that a greater dissolution rate of $\text{NO}_2\text{-N}_2\text{O}_4$ would have to be obtained before this disposal approach could be considered. Experiments were therefore conducted in which the N_2O_4 was delivered to the receiver using spargers with 10 to 15 micron porosity, to facilitate the production of small bubbles and thus allow a greater rate of dissolution. These experiments are described in the following section.

VI. VAPOR PHASE ADDITION OF N_2O_4 TO HOLDING PONDS.

1. Introduction

The preceding section describes experiments which were only partially successful because of limited dissolution rate. To improve on these results, and also to test the validity of the thermal analyses of Section I. A of the "Application Studies" portion of this report, a laboratory scale model of a holding pond disposal process in which N_2O_4 is introduced as small vapor bubbles was constructed.

2. Experimental Results

A 500 ml. r.b. flask was filled with 50 ml. of N_2O_4 . Two glass tubes were inserted in a rubber stopper and the stopper in turn inserted in the opening in the flask. These tubes were attached to two spargers (3 cm. in diameter) containing fritted glass outlets.* These spargers were in turn inserted into a receiver bath containing two liters of tap water in a crystallizing dish 10 cm. high and 19 cm. in diameter. Five hundred gms. of marble chips were layered on the bottom of the crystallizing dish (Fig. 32). The N_2O_4 was allowed to vaporize, pass through the tubes and spargers and into the water in the receiving vessel. All 50 ml. of N_2O_4 were added over five hours and the pH dropped from 8.1 to 1.2 with essentially no change in temperature. At the end of eight hours, the solution was essentially neutralized (Table XXX). In the second experiment, the N_2O_4 was heated with a water bath to 35°C to speed passage of N_2O_4 into the receiver. This time the pH changed from 8.1 to 1.1 in two hours and twenty minutes and again no rise in temperature was noted. At the end of three hours and twenty minutes, the pH was neutral (see Table XXXI). At no time in these experiments was a red gas observed above the liquid in the receiver. Only clear bubbling CO_2 was observed. A third experiment was conducted in which the marble chips were removed and 50 mls. of N_2O_4 was added to plain tap water through the same previously described system. At room temperature, the addition was complete in 400 minutes and the pH was less than 0. A slight rise in temperature was noted and again no red gas indicating NO_2 was observed emanating from the water in the receiver flask (Table XXXII). A fourth experiment was conducted in which a water bath at 35°C was used to heat

* porosity M - 10-15 microns

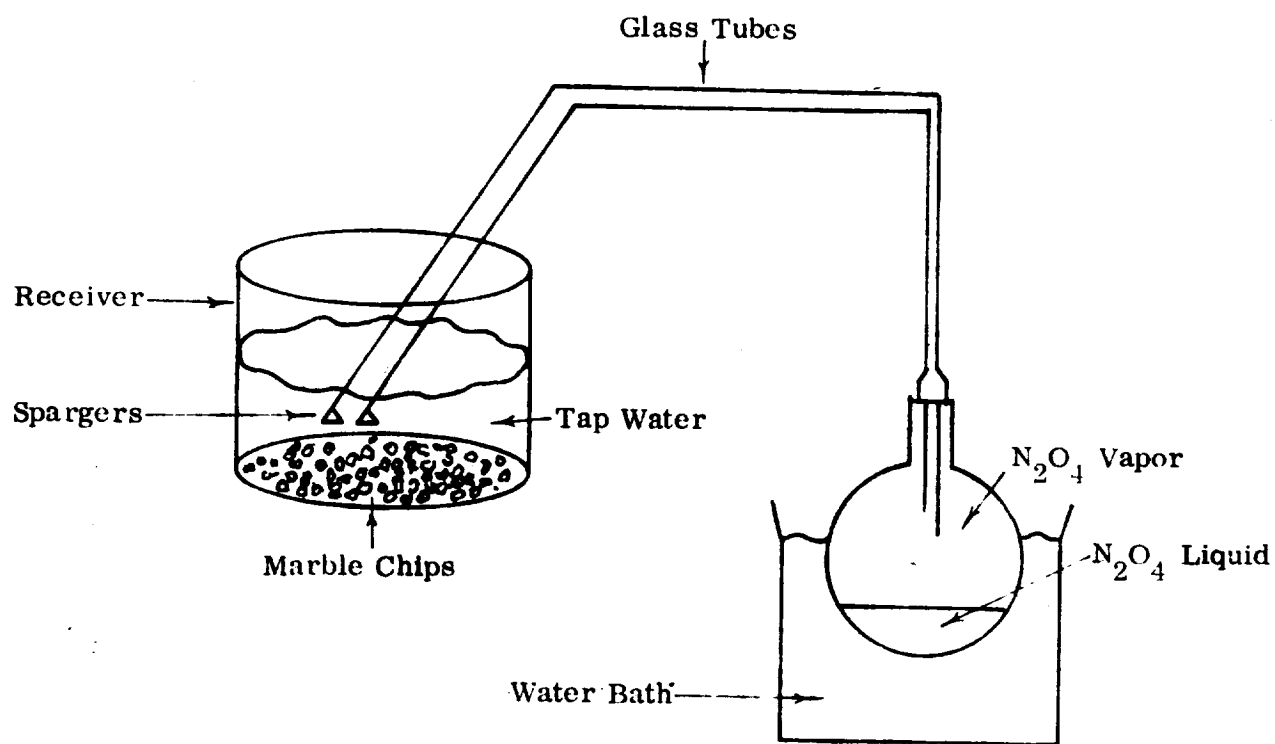


Figure 32. Laboratory model holding pond with vapor phase N_2O_4 addition.

TABLE XXX

Addition of N_2O_4 Vapor to Water and Calcium Carbonate at Room Temperature

<u>Time Mins.</u>	<u>pH</u>	<u>Receiver Temperature</u>	<u>Comment</u>
0	8.1	23.5	Start
10	8.0	23.5	NO_2 , N_2O_4 contacts water in receiver
20	3.0	23.0	CO_2 evolution starts
60	1.5	23.0	
300	1.2	23.0	End of N_2O_4 addition
480	6.6	23.5	End of CO_2 evolution

TABLE XXXI

Addition of N_2O_4 Vapor at 35°C to Water and Calcium Carbonate

<u>Time Mins.</u>	<u>pH</u>	<u>Receiver Temperature</u>	<u>Comment</u>
0	8.1	23.0	Start
10	6.5	23.0	NO_2 , N_2O_4 contacts water in receiver
30	1.2	22.5	CO_2 evolution starts
60	0.8	22.0	
120	0.8	22.0	
140	1.1	23.0	
200	7.1	23.0	End of CO_2 evolution

TABLE XXXII

Addition of N_2O_4 Vapor to Water at Room Temperature

<u>Time Mins.</u>	<u>pH</u>	<u>Receiver Temperature</u>	<u>Comment</u>
0	6.5	23.5	Start
15	2.5	23.5	
30	1.8	23.5	
60	1.5	23.5	
120	0.5	24.0	Receiver water has blue tint
400	< 0	25.0	End of N_2O_4 addition

TABLE XXXIII

Addition of N_2O_4 Vapor at 35°C to Water

<u>Time Mins.</u>	<u>pH</u>	<u>Receiver Temperature</u>	<u>Comment</u>
0	6.5	23.5	Start
15.0	1.5	24	
3.0	1.8	25	
120	< 0	26.5	End of addition of N_2O_4

the flask containing 50 ml. of N_2O_4 . This treatment resulted in a faster flow of N_2O_4 into the receiver vessel. The data are shown in Table XXXIII. Again, no red gas indicating NO_2 was observed above the water level in the receiver.

After completion of addition of N_2O_4 in these two experiments, each solution was neutralized with 500 ml. of 10% aqueous hydrazine. The results are shown in Table XXXIV. During neutralization vigorous gaseous effluence was noted but no brown gas was seen. After neutralization the solution had an amber color.

TABLE XXXIV

Addition of 10% Hydrazine Solution to 2.5% Aqueous Solution of N_2O_4

	<u>Experiment 3</u>	<u>Experiment 4</u>
Addition time	2.5 minutes	3.0 minutes
Temperature Increase	20°C	25°C
pH after addition	6.6	6.5

3. Discussion

It may be assumed that a 2.5% (vol./vol.) solution of N_2O_4 in water results in a solution of such high acidity as to pose a threat to the eyes of any person in the immediate vicinity of such a holding pond. Dilution would, of course, tend to neutralize but massive amounts of water would be required. Therefore, a holding pond containing dissolved N_2O_4 (actually HNO_3 and HNO_2) would have to be almost immediately neutralized with hydrazine fuels or another neutralizing agent such as limestone ($CaCO_3$) in order to render the solution innocuous. Using systems analogous to those devised in these experiments, it should be possible to dissolve a large amount of N_2O_4 vapor in water in a short period of time. Such dissolution is critically dependent upon the use of spargers containing small pores.

These experiments show that it is possible to neutralize N_2O_4 solutions with hydrazines, generating at least 20°C of heat, but still cause no release of any NO_2 .

These experiments also show conclusively that inexpensive undissolved marble chips can effectively neutralize N_2O_4 solutions in a relatively short period of time.

VII. OXIDATION OF DILUTED N_2H_4 BY OZONE BUBBLING

OBJECTIVE: To Study the Decomposition of N_2H_4 by Bubbling O_3 through a Diluted Solution.

1. Introduction

N_2H_4 , being a strong reducing agent, is subject to easy oxidation with an oxidizing agent. A powerful oxidant is ozone (O_3). In dilute solution the rate of reaction is controllable to prevent a runaway reaction either by limiting one of the constituents or by providing sufficient dilution to dissipate the heat of reaction. Thus, a system like this was thought to provide a possible waste fuel disposal method.

A search of available literature turned up no useful information. Therefore, these experiments were set up to explore the effectiveness of this disposal method.

2. Procedure

A series of 9 test runs were made. Samples of dilute N_2H_4 solution were poured into 500 ml. gas bubbling cylinders provided with a medium porosity gas sparger and a thermometer (Figure 33).

Dry O_2 from a commercial tank was piped through a flowmeter (set at 15 SCFH) to the ozone-generating apparatus. The output was bubbled through the N_2H_4 solution for 1-2 hours. Small samples (5-10 ml) were removed periodically and analyzed for residual N_2H_4 . The temperature of the solution was measured at 5-10 minute intervals. The analytical

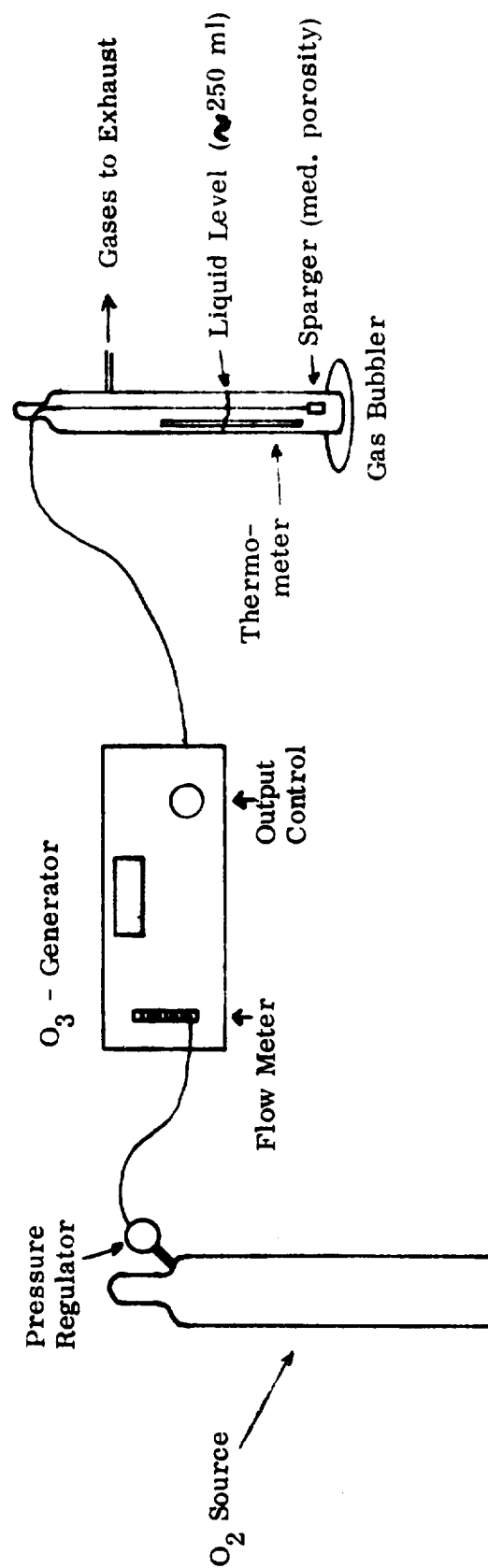


Figure 33. Experimental apparatus for O_3 bubbling tests.

method utilized p-DAB reagent as described in Appendix B. Ozone was analyzed using the o-tolidine reagent method after establishing a concentration curve.

Plots of the resulting data were made and are discussed below.

3. Results

The concentration and temperature vs. bubbling time are plotted in Figures 34 through 38. Ozone was added at a rate of 1.2 grams per hour in all tests.

As shown in Figure 34, tests 2, 3, and 4, approximately 0.5 % N_2H_4 is oxidized by O_3 in a controlled manner within a 2 hour period to about the 5 ppm concentration - a 99.9 % reduction.

As a comparison, in test 5, a similar N_2H_4 solution was reduced by air bubbling to the 3825 ppm level - a 24% reduction. Evaporation losses were not determined, but they may be assumed to be nearly identical for both set ups or slightly higher in test 5 due to initial preheating.

In test 6, the ozonation of a preheated solution was only very slightly less effective than in tests 1 through 4 - a 97.9 % reduction in 110 minutes. This is opposite to the anticipated quicker reaction at elevated temperature. This result was probably due to the more rapid disintegration (or lower solubility) of ozone in warm water. The shape of curve 6 corresponds closely with the shape of curve 7, resulting from a solution approximately 10 times stronger.

In Figure 35 are plotted the results of tests 7, 8, and 9 with solutions containing higher N_2H_4 concentrations. The curves do not follow any particular pattern. There may be yet undetermined variables affecting the ozonation. Alternately, the ozonator itself was misbehaving during these runs which may partly account for the variations.

In Figures 36 and 37 are plotted curves showing temperature as a function of bubbling time. The temperature increases as reaction proceeds, then levels off and finally drops when the N_2H_4 is reduced to a low level.

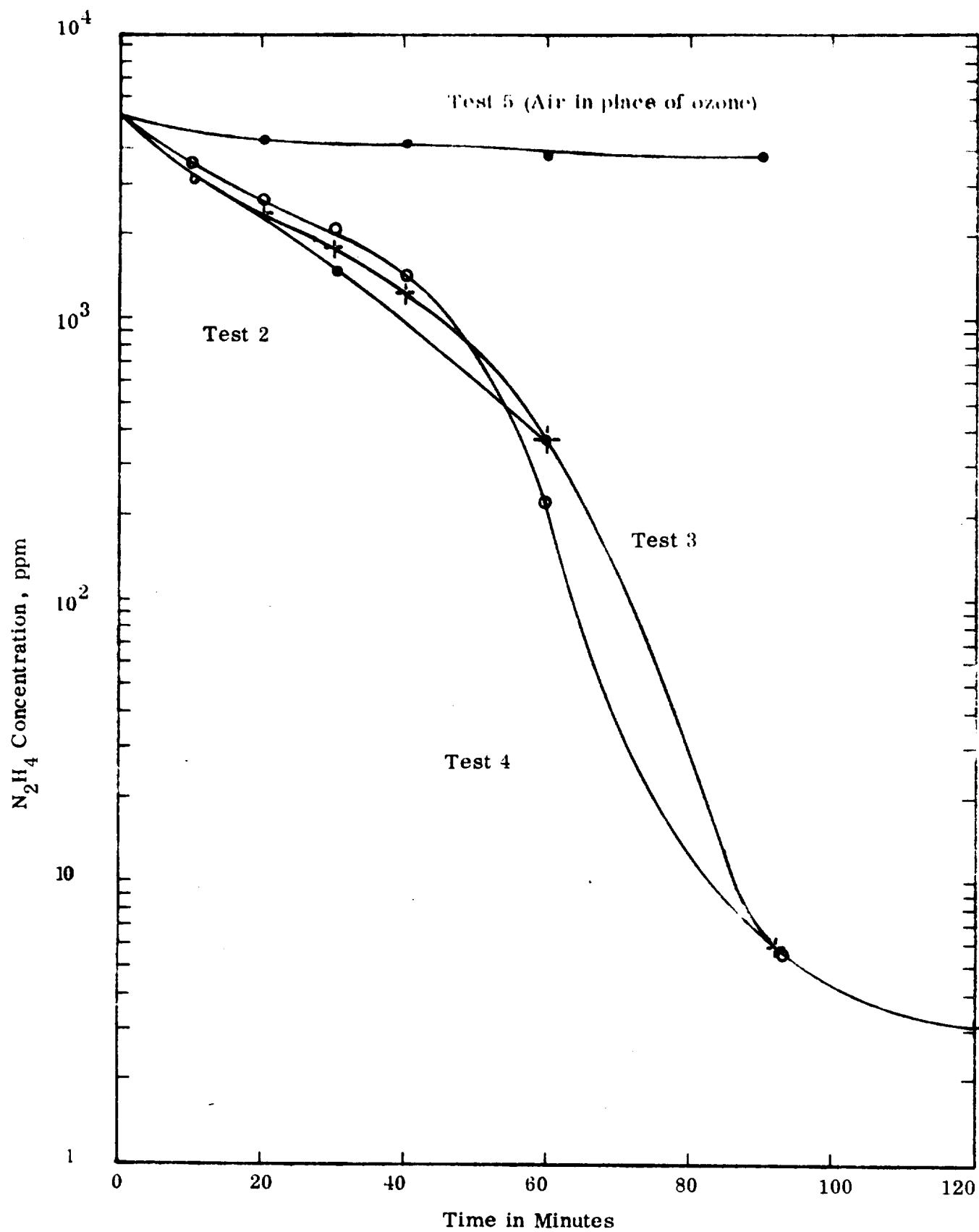


Figure 34. Ozonation and air oxidation of N_2H_4 : fuel concentration as a function of time.

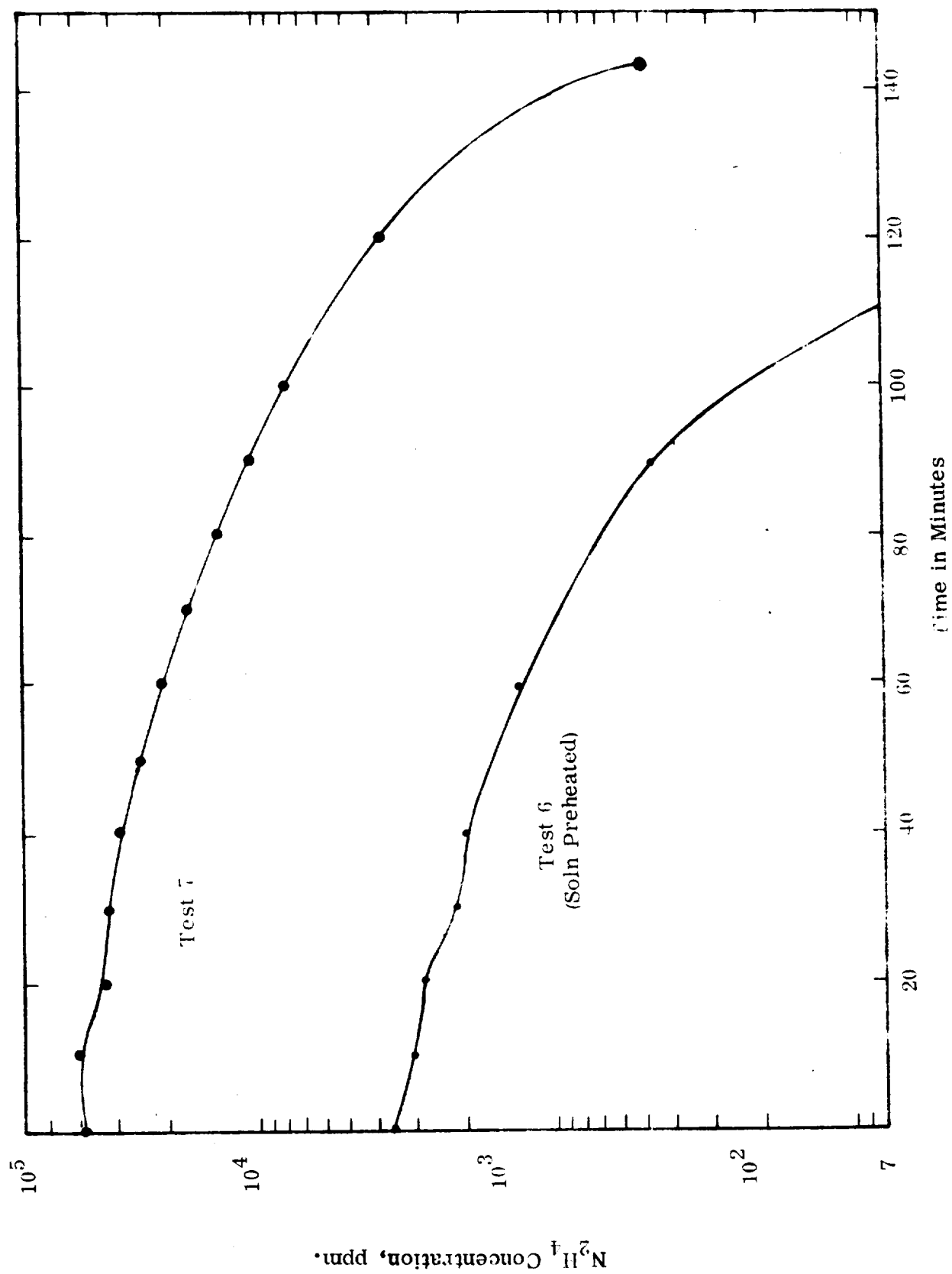


Figure 35. Ozonation of N_2H_4 : fuel concentration as a function of time.

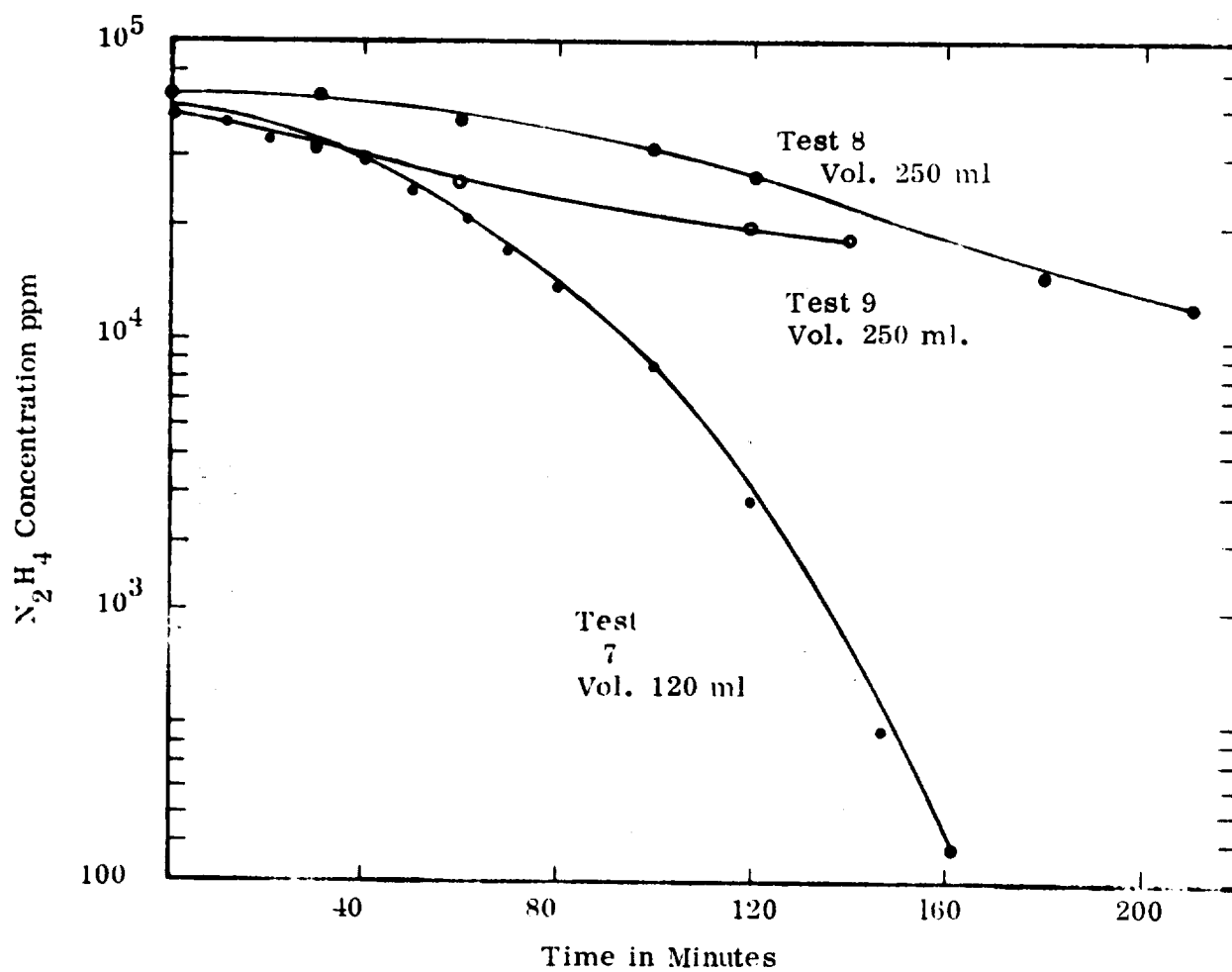


Figure 36. Ozonation of relatively concentrated solutions of N_2H_4 : fuel concentration as a function of time.

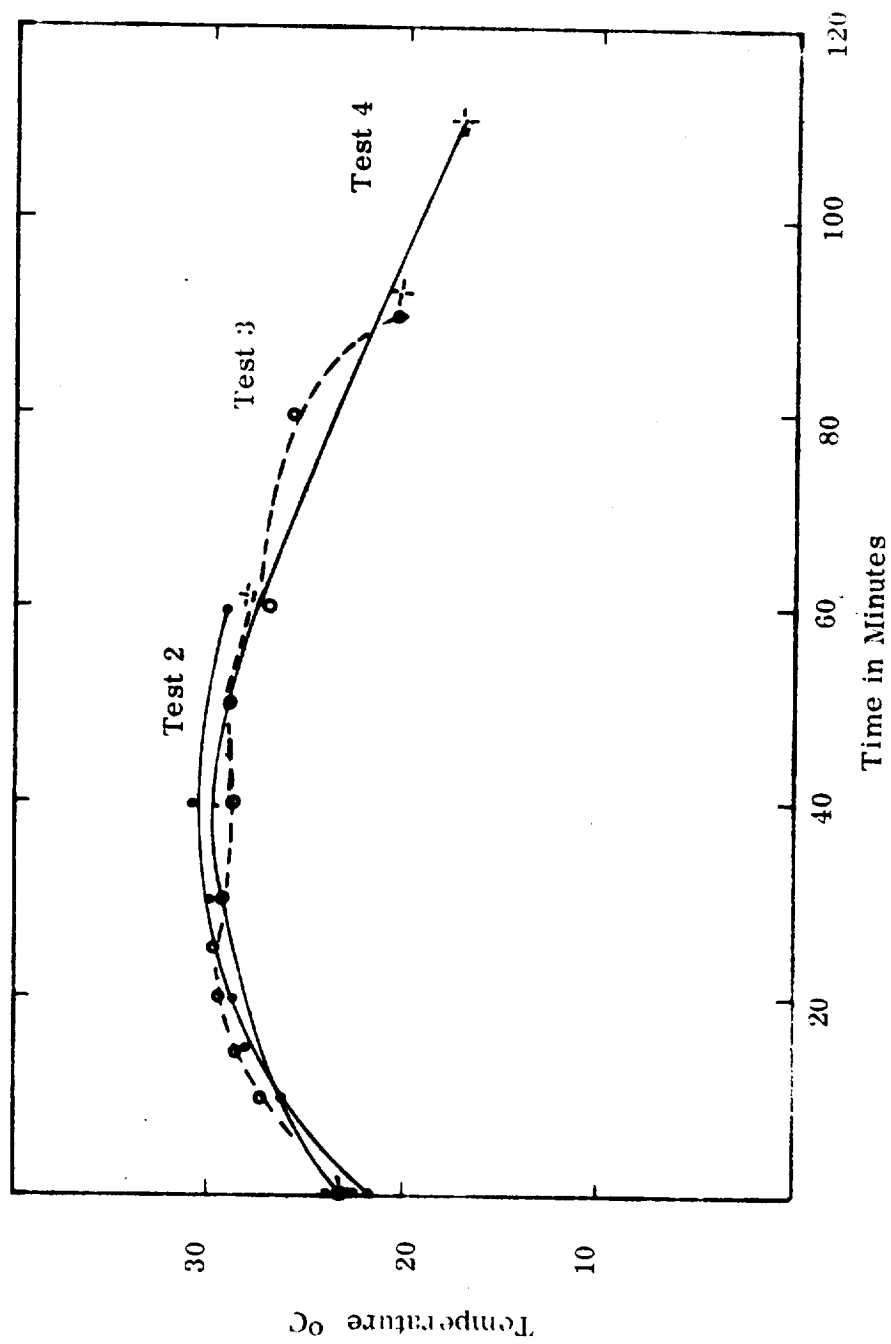


Figure 37. Temperature histories : N_2H_4 ozonation

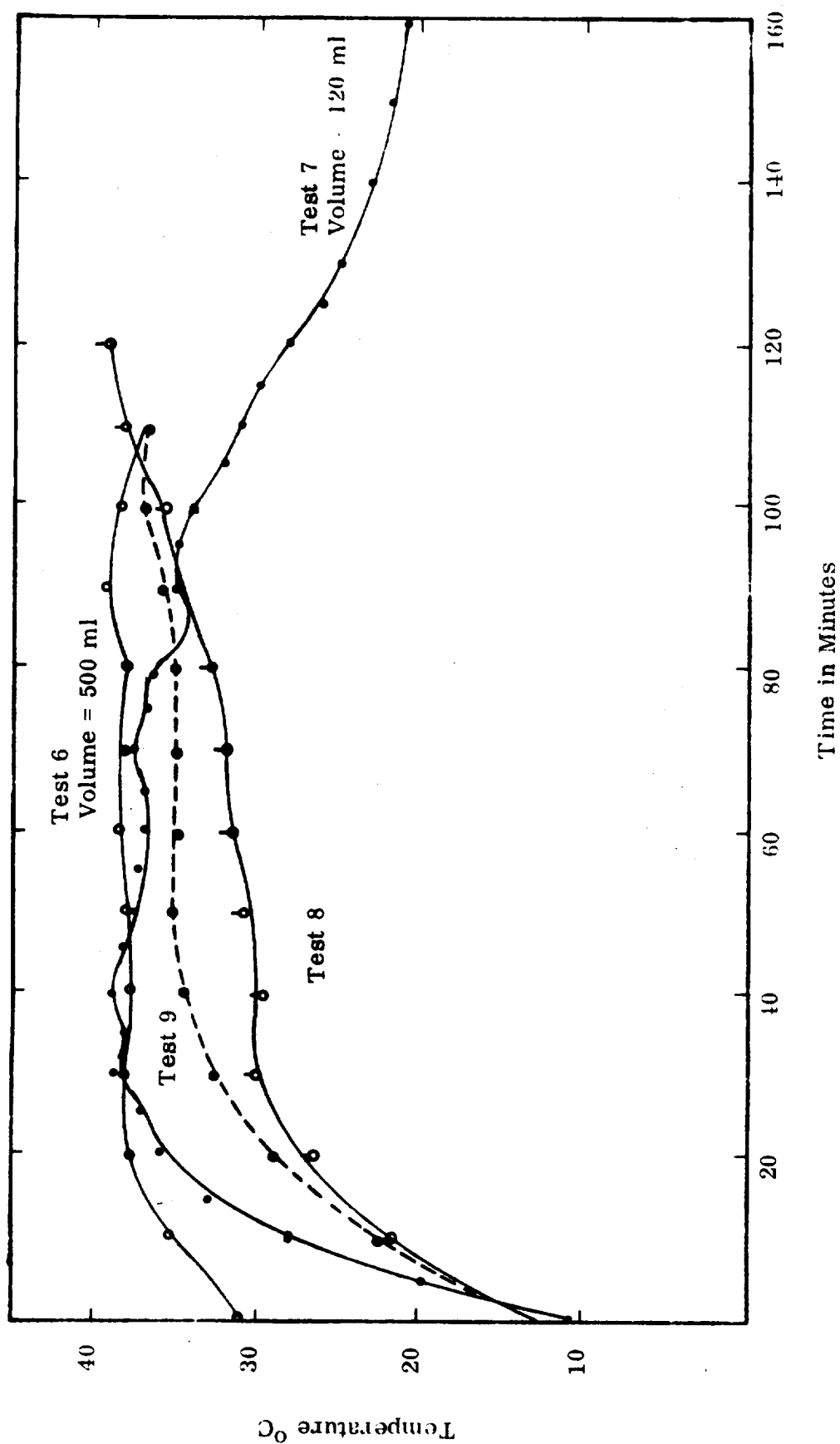


Figure 38. Temperature histories : N_2H_4 ozonation.

Table XXXV lists the stoichiometric O_3 requirements of the nine treated batches of N_2H_4 . The correspondence of these figures with the data of Figures 34 through 38 is established by the ozone flow rate, which was 1.2 grams (1200 mg) per hour. Thus, in test 8 approximately $(5130 / 1200) = 4.3$ hours would be required to generate enough O_3 to neutralize the initial N_2H_4 solution, if complete absorption occurred.

Table XXXVI shows O_3 concentration in distilled water after bubbling for the stated times. These figures indicate (very roughly) the O_3 concentration to be expected in the N_2H_4 solution. O_3 concentration was in the 1 ppm range during the bubbling treatment.

4. Discussion

The objective of this study was accomplished. The results show decomposition of N_2H_4 by O_3 is easily effected. For example, the concentration of N_2H_4 was reduced from 5000 ppm (.5 %) to below 10 ppm or lower within a short period of time (1-2 hours). More concentrated solutions (several %) can be reduced to low levels by allowing a longer treating period in order to control problems associated with the heat of reaction.

The gaseous output from the ozonator at the setting used was a mixture of O_2 and O_3 in approximate ratio of 1 part O_3 to 45 parts O_2 .

The temperature of the reaction was monitored during a run and the supply of O_3 could be immediately reduced or stopped, if necessary. Thus, reaction rate was controlled simply by limiting the supply of O_3 bubbled into the solution. Due to the low capacity of the O_3 generator (1.2 g/hr or .02 g/min) the quantity of heat released was only sufficient to raise the temperature a maximum of $28^{\circ}C$ above the ambient temperature in one run (Test 7). In no case did the temperature rise above $49^{\circ}C$. In solutions containing approximately 0.5% N_2H_4 , ΔT (the maximum temperature rise above ambient) did not exceed $10^{\circ}C$. In tests 7, 8, and 9 containing several % N_2H_4 , ΔT exceeded $20^{\circ}C$ as shown:

TABLE XXXV
OZONE REQUIREMENTS
(STOICHIOMETRIC)

Test #	Vol. of Solution ml.	Initial N_2H_4 Concn. ppm	O_3 Requirements mg	Comments
1	250	5,150	620	
2	250	5,150	620	
3	250	5,100	610	
4	250	5,100	610	
5*	250	5,070	810	Air Bubbling
6*	500	3,550	856	High Vol.
7	120	38,250	2200	Low Vol.
8	250	42,750	5130	
9	250	37,250	4420	

* Solution was preheated before introducing O_3 .

TABLE XXXVI
 CONCENTRATION OF O₃ IN DISTILLED WATER
 (Vol. = 250 ml)
 (lab. ambient
 temp.)

TIME OF BURBLING O ₃ min.	O ₃ CONCENTRATION (Average of 2 Determinations) (PPM)
5	.69
10	.80
20	.71
30	.60
40	1.12

Note: Lange's "Handbook of Chemistry" gives the following solubility data for O₃ in H₂O: 0.88 cc @ 0°C, 0 cc @ 60°C.

Test #	2	3	4	6	7	8	9
$\Delta T(^{\circ}\text{C})$	6 ⁰	9 ⁰	7 ⁰	8 ¹ ₀	28 ⁰	26 ⁰	24 ⁰

In the air bubbling experiment (Test 5) which was preheated to 45⁰C, a hot plate was necessary to maintain temperature above 40⁰ C.

In the chemical neutralization waste disposal methods utilizing chlorine-releasing compounds, severe equipment corrosion problems are often encountered. In all chemical neutralization methods the reagent and operational costs are high, and environmental hazards due to the quantities of reagent used might also be high. The O₃ bubbling method may offer a distinct advantage and should be investigated further.

The cost of generating O₃ for a small application is relatively high but not prohibitively so. For a large application, the cost of supplying O₃ would be somewhat higher than the cost of chlorine. Ozone is used in Europe for disinfecting water supplies.

Although O₃ bubbling runs were made only with N₂H₄, the idea is applicable to both MMH and UDMH, where the chemistry is not much different.

In summary, neutralization of N₂H₄ with O₃ appears to be a suitable method for disposal of waste N₂H₄.

5. Conclusions

The following conclusions were drawn:

- (1) O₃ bubbling was effective in oxidizing a 0.5% N₂H₄ solution to below the 10 ppm level within 2 hours.
- (2) The temperature rise resulting from heat of reaction was easily controlled by restricting the O₃ supply to the solution.
- (3) The O₃ bubbling method should be considered as having potential application where chemical neutralization methods are currently used.

APPLICATION STUDIES (PHASE 3)

	Page
I. Introduction.....	229
II. Fuel-Oxidizer Reactions in Dilute Solutions.....	230
A. Thermal aspects of holding ponds	230
B. Neutralization of diluted hydrazines with diluted oxidizers	234
C. Neutralization of 5% hydrazine solutions using vapor phase nitrogen tetroxide	239
III. Aeration Ponds for Hydrazine	240
A. Air oxidation of diluted fuels with or without catalysts	242
B. A discussion of air bubble growth, detachment, and rise	249
IV. Scrubbers	270
V. Precipitation of Fluoride from Diluted IRFNA Solution	279
VI. Fume Hood Design Considerations.....	281
VII. Waste Handling and Facility Location Considerations.....	285
A. Sources of, and disposal sites for, space shuttle hypergolic propellant wastes	285
B. Rough cost estimates for transportation of hypergolic wastes from collection to disposal sites	295
C. Dumping of hypergolic propellants from drum type containers	298
VIII. Aspects of Disposal at Contingency Landing Sites	303

I. INTRODUCTION

The second category of studies undertaken in Phase 3 involved engineering analysis and design considerations relating to the application of various disposal methods. Some of these studies were related to certain particularly attractive disposal methods, while others were concerned with specific disposal situations.

Among disposal methods, there was particular interest in oxidation ponds and fuel-oxidizer reaction ponds, as both of these facilities were found in the evaluation phase to be especially effective and economical means of disposing of liquid propellants and scrubber discharge liquids without creating secondary environmental hazards. Analytical and experimental studies treated thermal aspects of the diluted fuel-oxidizer reaction to aid in establishing design criteria for actual ponds. Minor variations on existing neutralization methods - the use of urea as a neutralizing agent for oxidizers, and of acetic acid to neutralize the fuels - were investigated in conjunction with the thermal studies. Experiments were also performed to establish design criteria for oxidation ponds, by measuring hydrazine concentrations as a function of time in an aerated pond, and by looking at the effects of copper and iron catalysts on these results. A thorough study of the literature on bubble growth and detachment was undertaken as a basis for aerator design - the effects of various materials and pore sizes, the pumping requirements, and other important parameters were considered. Scrubbers were studied in terms of establishing guidelines for selecting sizes and flow rates, and particular attention was given to counter current scrubbers. The question of HF removal from dilute IRFNA solutions, which was not completely resolved earlier in the study (partly because of the current lack of IRFNA disposal activities) was examined experimentally.

A number of specific disposal problems were also studied, including fume hoods in which small assemblies containing residual propellants could be disassembled, and systems for the remote dumping of hypergolic fuels from drum-type containers. Facility location considerations for various disposal situations, including considerations of alternate or contingent landing sites, were treated.

II. FUEL-OXIDIZER REACTIONS IN DILUTE SOLUTIONS

Several methods for the neutralization, dilution or decomposition of hypergolic propellants involve the use of holding ponds. The advantages of holding ponds include ease of construction, low installation cost and ease of operations. Possible disadvantages include leakage from the pond, which might contaminate local water supplies. Modern high performance coatings or films will probably preclude leakage, subject perhaps to periodic replacement, and might be required.

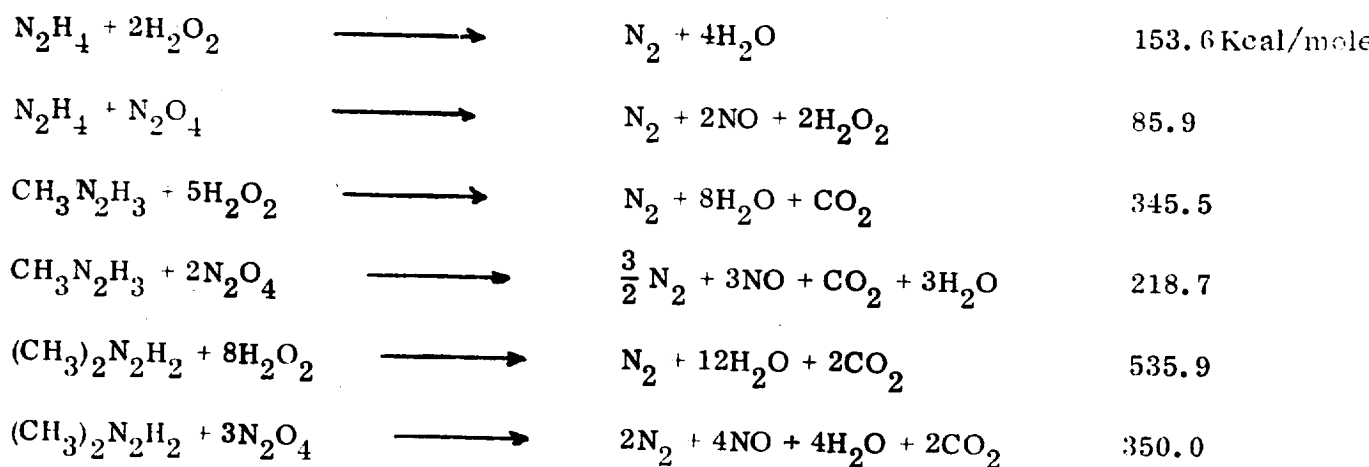
Questions of concern in the design of holding ponds include thermal considerations: how rapidly can fuel and oxidizer be added to a pond without causing pond temperature to rise to a point that would either be particularly hazardous, or cause significant amounts of toxic vapors to be evolved. These considerations are important in establishing minimum sizes of ponds for various applications. The following pages describe three separate studies that were carried out to provide answers to these and related questions.

A. THERMAL ASPECTS OF HOLDING PONDS

A small rectangular pond, 30 meters (100 ft) long, 20 meters (66ft) wide and 1 meter (3.3 ft) deep, was arbitrarily chosen for purpose of calculations. The depth of one meter (3.3 ft) was chosen to avoid digging into the water table. Also, it would allow anyone accidentally falling into the pond to easily walk out.

Construction of the pond consists of excavating a hole to the proper dimensions and lining it with a suitable material, such as concrete and a sealant, plastic, or stainless steel.

In the holding pond, fuel and oxidizer can be mixed in the proper ratios to neutralize one another. The chemical reactions are exothermic (heat given off) and the temperature of the pond will increase. The heats of reaction for the various reactions of interest (for initial and final states at Standard Temperature and Pressure) are as follows:



a. Transient Calculation

A temperature increase of 30°C was arbitrarily chosen for purposes of calculation. If a large quantity of fuel and oxidizer is rapidly mixed in the pond, assuming for the time being that there is no heat loss, the amount of fuel plus oxidizer that would raise the temperature of the pond 30°C can be calculated using the heats of reaction, pond dimensions, and heat capacity of water to give the following results:

International Standard Units	English Units
$3.75 \times 10^3 \text{ Kg N}_2\text{H}_4 + 7.85 \times 10^3 \text{ Kg H}_2\text{O}_2$	$1.01 \times 10^3 \text{ gal N}_2\text{H}_4 + 1.52 \times 10^3 \text{ gal H}_2\text{O}_2$
$6.50 \times 10^3 \text{ Kg N}_2\text{H}_4 + 18.6 \times 10^3 \text{ Kg N}_2\text{O}_4$	$1.7 \times 10^3 \text{ gal N}_2\text{H}_4 + 3.40 \times 10^3 \text{ gal N}_2\text{O}_4$
$2.40 \times 10^3 \text{ Kg MMH} + 8.85 \times 10^3 \text{ Kg H}_2\text{O}_2$	$7.35 \times 10^2 \text{ gal MMH} + 1.67 \times 10^3 \text{ gal H}_2\text{O}_2$
$3.80 \times 10^3 \text{ Kg MMH} + 15.20 \times 10^3 \text{ Kg N}_2\text{O}_4$	$1.15 \times 10^3 \text{ gal MMH} + 2.80 \times 10^3 \text{ gal N}_2\text{O}_4$
$2.00 \times 10^3 \text{ Kg UDMH} + 9.06 \times 10^3 \text{ Kg H}_2\text{O}_2$	$6.85 \times 10^2 \text{ gal UDMH} + 1.75 \times 10^3 \text{ gal H}_2\text{O}_2$
$3.14 \times 10^3 \text{ Kg UDMH} + 14.5 \times 10^3 \text{ Kg N}_2\text{O}_4$	$1.05 \times 10^3 \text{ gal UDMH} + 2.64 \times 10^3 \text{ gal N}_2\text{O}_4$

b. Steady State Calculation

Next we consider the propellant flow rates necessary to maintain a constant temperature difference of 30°C between the pond and its surroundings. For steady state, the energy released by the reaction of the propellants

entering the pond will just equal the heat transfer from the pond to the surroundings.

The heat transfer from a pond at temperature ΔT above ambient is considered to be the sum of a convective part and a conductive part. The conductive part is approximated by the conduction from a source of radius equal to mean pond dimensions, on the surface of an infinite half-space. The free convection from the pond is assumed to be laminar for the sake of obtaining a conservative result. Any heat flow due to the evolved gases of the reaction leaving the pond has been ignored. This heat flow may be significant; thus the calculation is conservative. The heat transfer is then¹

$$\begin{aligned}\frac{dQ}{dt} &= \frac{dQ_{\text{COND}}}{dt} + \frac{dQ_{\text{CONV}}}{dt} \\ &= f(\text{geometry}) k \Delta T + hA \Delta T \\ &= \frac{4\pi k \Delta T}{\frac{1}{r_i} - \frac{1}{r_o}} + .27 \left(\frac{\Delta T}{L} \right)^{.25} A \Delta T\end{aligned}$$

where r_i = mean radius of pond = $\frac{L + W}{2}$

$$r_o \rightarrow \infty$$

The resulting rates at which the fuel and oxidizer can be mixed in order to maintain a steady state are as follows:

-
1. Eckert, E. R. G. and R. M. Drake, Heat and Mass Transfer, Second Edition, McGraw-Hill, New York, 1959, Eqn. 3-10

International Standard UnitsEnglish Units

1.22 $\frac{\text{Kg}}{\text{hr}}$ N_2H_4 + 2.60 $\frac{\text{Kg}}{\text{hr}}$ H_2O_2	.31 $\frac{\text{gal}}{\text{hr}}$ N_2H_4 + .53 $\frac{\text{gal}}{\text{hr}}$ H_2O_2
2.10 $\frac{\text{Kg}}{\text{hr}}$ N_2H_4 + 6.02 $\frac{\text{Kg}}{\text{hr}}$ N_2O_4	.55 $\frac{\text{gal}}{\text{hr}}$ N_2H_4 + 1.1 $\frac{\text{gal}}{\text{hr}}$ N_2O_4
0.78 $\frac{\text{Kg}}{\text{hr}}$ MMH + 2.99 $\frac{\text{Kg}}{\text{hr}}$ H_2O_2	.23 $\frac{\text{gal}}{\text{hr}}$ MMH + .60 $\frac{\text{gal}}{\text{hr}}$ H_2O_2
1.23 $\frac{\text{Kg}}{\text{hr}}$ MMH + 4.93 $\frac{\text{Kg}}{\text{hr}}$ N_2O_4	.37 $\frac{\text{gal}}{\text{hr}}$ MMH + .88 $\frac{\text{gal}}{\text{hr}}$ N_2O_4
0.65 $\frac{\text{Kg}}{\text{hr}}$ UDMH + 2.96 $\frac{\text{Kg}}{\text{hr}}$ H_2O_2	.22 $\frac{\text{gal}}{\text{hr}}$ UDMH + .95 $\frac{\text{gal}}{\text{hr}}$ H_2O_2
1.02 $\frac{\text{Kg}}{\text{hr}}$ UDMH + 4.70 $\frac{\text{Kg}}{\text{hr}}$ N_2O_4	.34 $\frac{\text{gal}}{\text{hr}}$ UDMH + .84 $\frac{\text{gal}}{\text{hr}}$ N_2O_4

It should be noted that these figures would not increase were the depth of the holding pond increased, but would rise in almost direct proportion to the surface area of the holding pond. Thus, the proportions of the pond will be determined by its use: whether it is subjected to occasional large dumps or to a steady flow of hydrazine fuels.

B. NEUTRALIZATION OF DILUTED HYDRAZINES WITH DILUTED OXIDIZERS

OBJECTIVE: To observe the ΔT (peak) on mixing hydrazines with oxidizers at various concentrations.

1. Introduction

A brief series of laboratory experiments was run on the temperature rise involved in neutralization of small quantities of diluted hydrazines with diluted oxidizers. The concentration of reactants was from 1 to 20%. It was desired to determine if a prohibitively high temperature rise occurred on mixing fairly strong concentrations. If temperature rise was not excessively high, it was reasoned that storage volume and equipment sizes could be made smaller by designing for relatively high concentrations. Selection of the highest concentration known to be safe will be helpful in choosing the minimum size storage volume required for equipment or holding ponds for at least partial self-neutralization.

There probably exist many records in various labs on similar experiments, but none were available to us when we sought them. It was decided that less time would be spent in actually doing the work required than in asking for information from a number of scattered organizations.

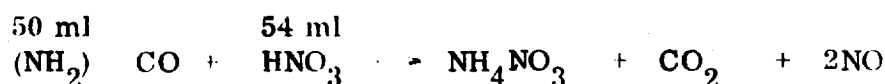
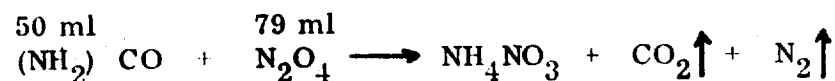
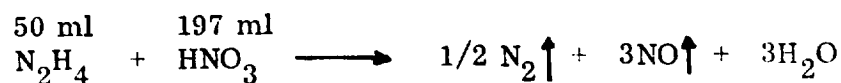
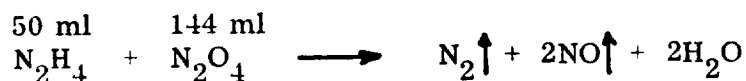
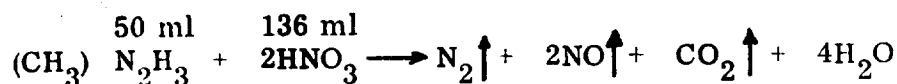
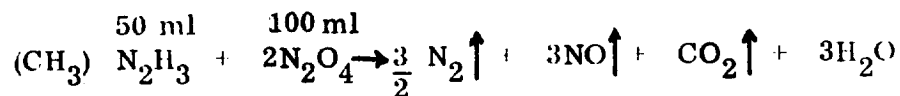
2. Procedure

Solutions of MMH, N_2H_4 , N_2O_4 , IRFNA, urea and acetic acid were prepared in various concentrations. These generally included 20%, 10%, 7 1/2%, 5% and 1% by weight.

A volume of 50 ml of each reducer (MMH, N_2H_4 or Urea) was poured into a beaker confined within a fume hood. The temperature of the solution was noted. The entire measured volume of diluted oxidizer (N_2O_4 or IRFNA) corresponding to the stoichiometric requirement was poured at once into the beaker. The beaker was swirled by hand and agitated with a thermometer to mix the reactants. The peak temperature attained was observed and recorded as ΔT (peak temperature minus initial temperature). No allowance was made for heat absorption by the beaker or heat losses to the atmosphere.

3. Equations for the Reactions

The volumes of solutions used appear above each reactant.



4. Results

Figure 39 shows the temperature rise encountered by intermingling stoichiometric quantities of diluted solutions in a 500 ml beaker to approximately 100 to 250 ml combined volume. In the stronger concentrations the ΔT exceeded 20°C . In the lowest concentration the ΔT was from undetectable to 4°C .

In comparing the ΔT of these reactions it is observed that N_2H_4 yields a higher ΔT with any of the oxidizers than does MMH. Also, with either hydrazine, N_2O_4 produces a higher ΔT than IRFNA. Again, N_2O_4 yields a higher ΔT with urea than does IRFNA.

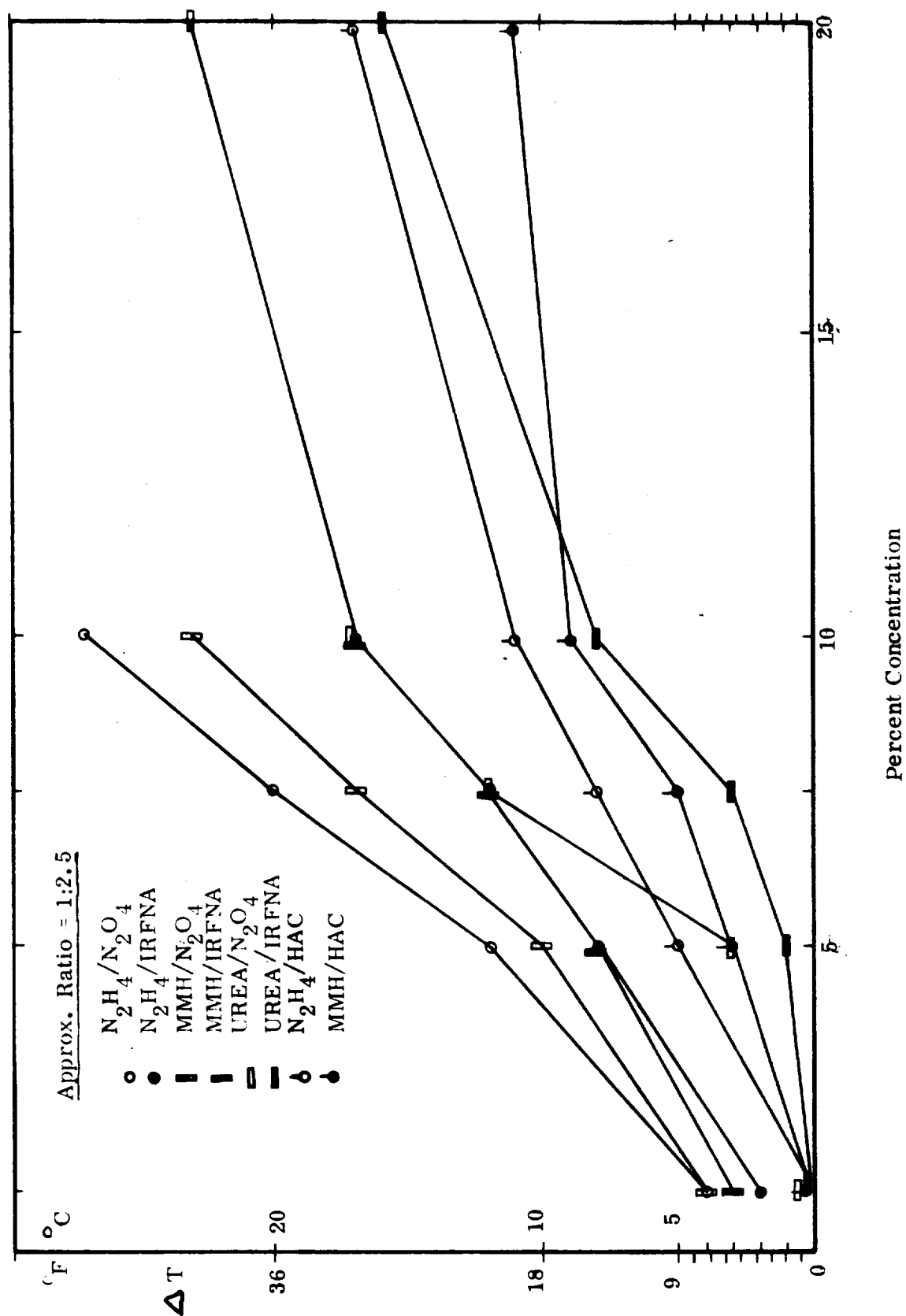


Figure 39. ΔT vs. concentration for stoichiometric reactions in solutions.

The amount of gas evolved was copious in reactions of N_2O_4 or IRFNA with either hydrazine; more so with N_2O_4 than with IRFNA.

There was considerable gas evolution in reacting N_2O_4 or IRFNA with urea.

There was little or no gas evolved when reacting either hydrazine with acetic acid (HAc), although some bubbles formed on the sides of the beaker after mixing. The rise in temperature indicated chemical reaction.

Naturally, as weaker concentrations were mixed, there was decreased gas evolution and lower ΔT .

5. Discussion

The practical application of these data point to the following possibilities:

1. The relatively modest ΔT at 1 to 5% concentrations leads to the possibility that diluted oxidizers and diluted hydrazine (up to 5% each) may be indiscriminately mixed together provided they are mixed in an open system. (Not in a closed tank where copious gas evolution may induce high pressures). A ΔT of $10^\circ C$ above ambient is not excessive. No fire or explosion hazards would be created. There appears to be little danger of thermal runaway reactions occurring. Such a statement applies as well to larger volumes than those used in the lab tests.

Application of this information can be made to the design of holding ponds and open containers. One pond may serve for disposal of both types of wastes - hydrazines and oxidizers. Utilizing the dilution feature, one pond can accommodate wastes of any concentration.

2. The ΔT on mixing 7 1/2 % concentrations varies from about $20^\circ C$ for the hydrazine/oxidizer combination to about $3^\circ C$ - $12^\circ C$ for the urea oxidizer and hydrazine/acetic acid combinations.

3. For concentrations 10% or 20% the ΔT will be from $10^\circ C$ to $27^\circ C$ or higher if mixed at once. Direct mixing of hydrazines with oxidizers should be prohibited at such high concentrations except under carefully specified conditions by experienced personnel.

4. Mixing of one diluted hydrazine with another diluted hydrazine is believed to be feasible (or one type diluted oxidizer with another type diluted oxidizer) without involving hazards. (Such feasibility was not demonstrated in this study).

5. If one reactant is in excess, the resulting ΔT will be lower than that shown in Figure 39. The stoichiometric case is the worst.

6. After the initial gas evolution is completed for the main reaction, additional gas evolution continues in some cases due to completion of side reactions. Therefore, storage of mixed hydrazines/oxidizers is unsafe in closed systems for an undetermined period of time. No unsafe condition exists for storage of mixed wastes in open containers or ponds, except for the usual toxicity of reaction products such as NO_3^- .

6. Conclusions

1. This work was of an exploratory nature to determine ΔT obtained on mixing various combinations and concentrations of hydrazines and oxidizers, and of hydrazines with acetic acid and oxidizers with urea.

2. From these data, suggestions were made regarding the possibility of reducing the size of storage facilities for wastes by permitting mixing of concentrations up to 5% of fuels and oxidizers.

C. NEUTRALIZATION OF 5% HYDRAZINE SOLUTIONS USING VAPOR PHASE
 NITROGEN TETROXIDE

Holding ponds have been considered as methods of disposal for both hypergolic fuels and oxidizers. To determine the feasibility of this disposal system if N_2O_4 - NO_2 vapor is introduced directly into the holding pond, the following experiments were conducted.

A one liter solution of hydrazine NH_2NH_2 (5%) was prepared. The temperature was 27°C and the pH was 11.1. Fifty ml. of N_2O_4 was distilled into this solution through a sparger over a three hour period. The temperature rose to 32°C and a final pH of 7.7 was obtained, as expected since the hydrazine is in excess (mole ratio hydrazine to N_2O_4 is 1.7 to 1). No red NO_2 vapor was seen over the receiving solution.

A similar experiment using MMH was conducted. A 5% MMH solution was prepared (pH 10.5, temp. 28°C). 50 mls. of N_2O_4 were added over a two hour period and the temperature rose to 39°C while the pH declined to 7.2. The mole ratio of MMH to N_2O_4 in this case is 1.1 to 1. Again, no red cloud was observed.

It is concluded that disposal of vaporous N_2O_4 into dilute hydrazine solutions seems to be a safe and effective method of disposing of both these hypergols.

III. AERATION PONDS FOR HYDRAZINE

In the portion of this report concerned with "Evaluation of Current Disposal Methods," we discussed the reaction of fuels and oxidizers with various neutralizing reagents. All of these chemical methods are expensive, and involve secondary disposal problems in that non-toxic but environmentally hazardous compounds are introduced in large quantity.

It is partly for this reason, and partly for the purpose of evaluating new or lesser known methods of waste propellant disposal, that the air oxidation method was investigated. The objectives were additional familiarity with the method, and establishment of various design criteria and guidelines.

Visits by study personnel were made to the Western Test Range at Vandenberg Air Force Base, Johnson Space Center, and White Sands Proving Ground to observe existing oxidation ponds first hand and talk with engineers responsible for their design, maintenance and operation. The only operational aeration pond was at Johnson Space Center, where a very large flow of air is introduced through two H-shaped manifolds at the bottom of a fairly deep concrete holding pond. The bubbles generated are quite large, and result in a general roiling motion of the central part of the pond and visible circulation throughout most of the pond. At the Western Test Range, a spray pond has been constructed for experimental purposes, and one batch of hydrazine has been oxidized in the pond for data collection purposes. Oxidation ponds at White Sands Proving Ground are essentially untreated holding ponds, with air oxidation taking place naturally at the surface but no aeration.

Measurements at both Western Test Range and Johnson Space Center show that during aeration a period of time passes in which dissolved oxygen levels in the water increase, but there is no significant reduction in hydrazine level; this period is followed by a reduction in hydrazine content once the dissolved oxygen reaches saturation.

Operating experience at the one operational holding pond has apparently been quite satisfactory. It should be noted, however, that very little hydrazine disposal has taken place at JSC during the time (several months) that the aerator has been installed in this pond. The primary reason for installation was to provide a means of quickly oxidizing the hydrazine in case of emergencies - the need for pumping water from the pond to prevent overflow during very rainy weather, for example.

Starting with a 300 ppm N_2H_4 concentration in 0.5 million gallons of water, the hydrazine concentration can be reduced to 5 ppm in about twenty hours, with most of the reduction occurring in the last two to three hours. The addition of copper sulfate or iron oxide as a catalyst contributes to the speed of oxidation.

In the experiment at WTR, mixed hydrazine fuels were added to 50,000 gallons of water to a level of 120 ppm, with 0.2 mg/l copper ion as catalyst. The mixture was then sprayed into the air at a rate of 60 liters per minute for eleven days, achieving dissolved oxygen saturation, and allowed to sit. The hydrazine disappeared slowly thereafter, with oxidation essentially complete after another nine days. There was no significant emission to the atmosphere - only trace amounts of UDMH could be detected at a point six inches above the pond surface, except for one 6 ppm reading made thirty minutes after hydrazine transfer to the pond.

With these results in mind, a series of experiments was conducted to look at the effect of various parameters on the speed and cost effectiveness of hydrazine oxidation by air bubbling. In addition, a thorough review of bubble formation, growth and detachment was carried out, and past experiments and analyses of bubble rise velocities were reviewed.

A. AIR OXIDATION OF DILUTED FUELS WITH OR WITHOUT CATALYSTS

1. Procedure

Two 10 gallon aquariums were half-filled with tap water. Measured amounts of N_2H_4 or MMH were added, up to approximately 925 ppm. Either $CuSO_4$ or Fe_2O_3 or both were introduced as catalyst in the desired quantity. Three spargers located near the bottom of each tank were connected to the pressure end of a Gast pump to provide agitation. Air flow was approximately 2 l/min through each sparger. Residual concentration of material was determined daily for run durations of 1 to 9 days. The tanks were loosely covered with aluminum foil to minimize evaporation losses.

Analysis of the hydrazines was performed using p-dimethylamino benzaldehyde (see Appendix B). Chlorine demand, pH and dissolved oxygen measurements were performed in a few cases.

2. Results

Tests 1 and 2

Figure 40 shows that the rate of decomposition of N_2H_4 is considerably higher when using .02mg/l Cu^{++} catalyst than without the catalyst. Without the catalyst the oxidation of N_2H_4 proceeded slowly in spite of ample air bubbling and good agitation in the tank.

Test 3

Figure 41 shows that the Fe_2O_3 catalyst is not as effective in increasing the rate of N_2H_4 decomposition as the Cu catalyst.

Tests 4 and 6

Both tests show a rapid decomposition rate, starting with over 300 ppm N_2H_4 and being reduced to 1 ppm in one day.

Test 5

The curve shows rapid decomposition of N_2H_4 in the first day. The run was discontinued when the air hose disconnected during the run.

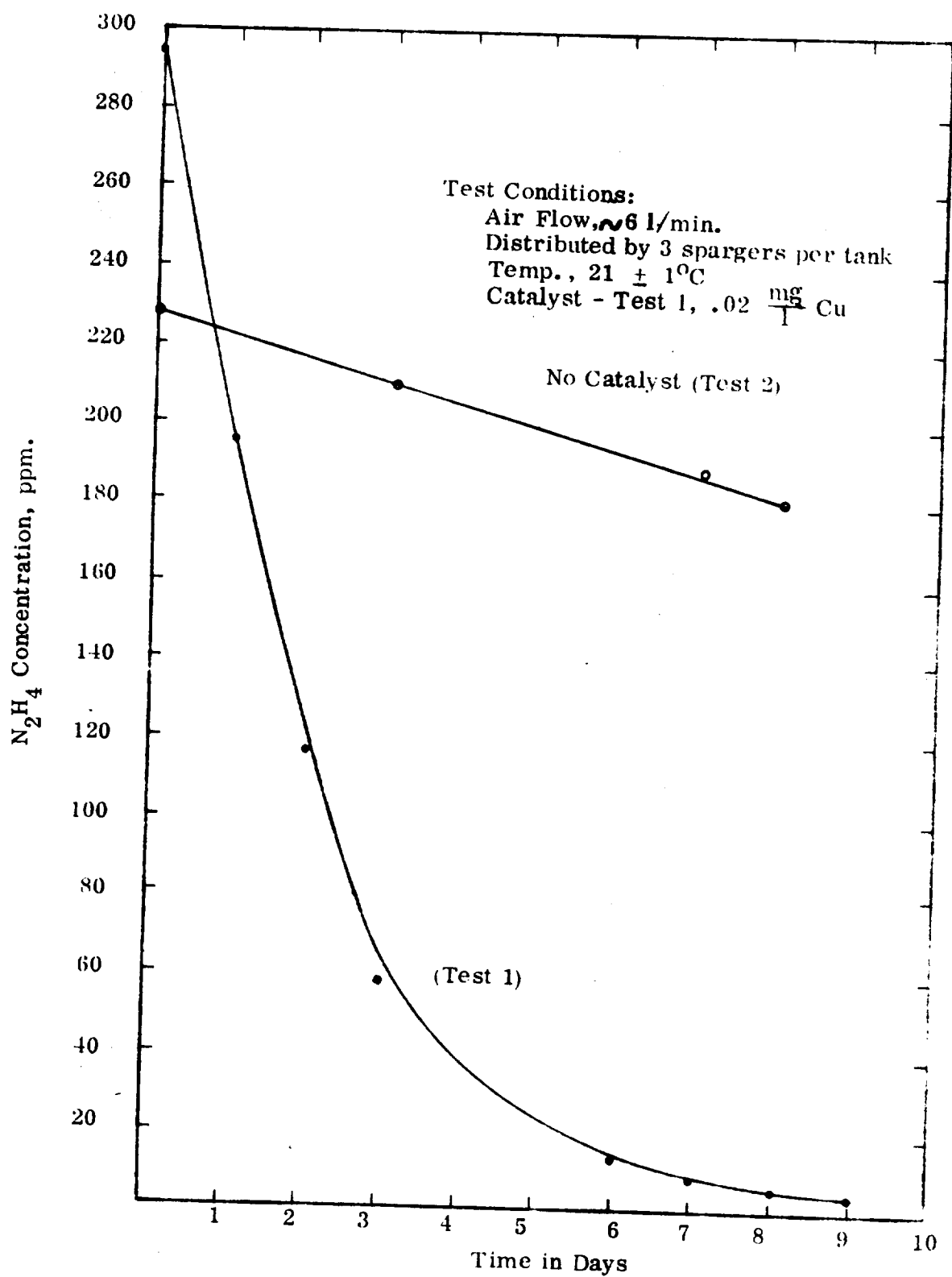


Figure 40. Air oxidation of N_2H_4 , Tests 1 and 2.

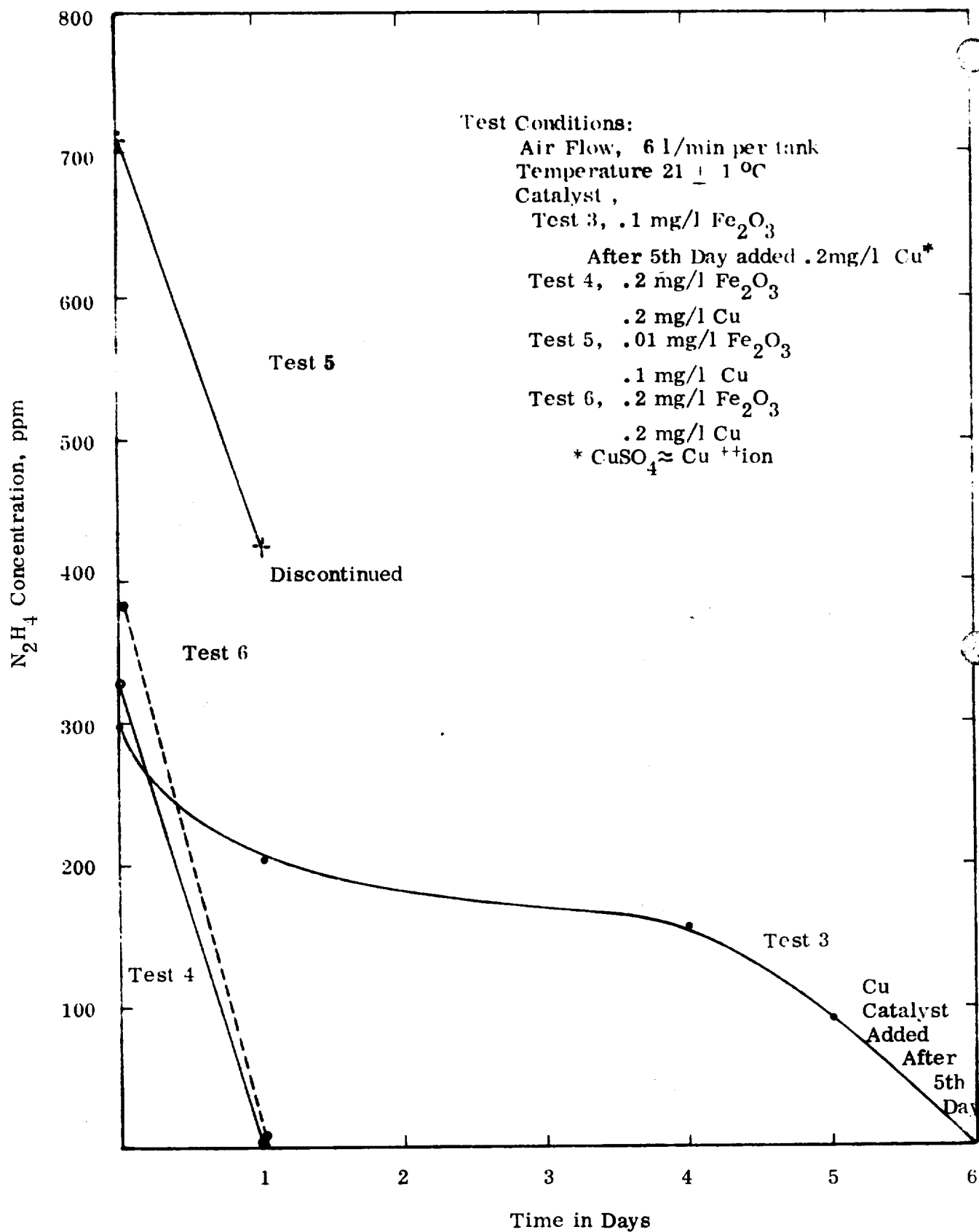


Figure 41. Air oxidation of N_2H_4 , Tests 3 through 6.

Tests 7 and 8

Figure 42 shows that the decomposition of N_2H_4 was rapid when using either Cu or Cu/Fe catalysts. The test was not conclusive in deciding on the more efficient catalyst. Almost complete disappearance of N_2H_4 occurred after 2 days of air treatment with either catalyst, starting with high concentrations.

Tests 9a and 9b

Figure 43 shows high rates of decomposition of the hydrazines. The MMH decomposes more slowly than N_2H_4 .

3. Discussion

Tests 1 and 2 demonstrate the advantage in using a catalyst to hasten decomposition of N_2H_4 .

In Test 3, the Fe_2O_3 was insoluble and most of it settled to the bottom of the tank. Therefore, contact opportunity was considerably lessened. This fact may account for the relatively lower decomposition rate of N_2H_4 in this run.

Tests 4 and 6 are exceedingly interesting due to the very rapid decomposition rate demonstrated. Given a large enough pond to effect sufficient dilution, with adequate air bubbling capacity, it is conceivable that waste N_2H_4 /MMH can be economically oxidized within a few days in an environmentally acceptable manner. Economical operation is expected as a result of low maintenance and equipment costs, few chemicals, and low labor requirement. The products are mostly N_2 with traces of NH_3 or other gases. The pond water can be reused and evaporation losses made up if rainfall is insufficient. The contained Cu ion will act as an algaecide.

An odor of NH_3 or amine was noticed in the vicinity of the tank for 1 or 2 hours after adding hydrazine. No air sample was taken to ascertain the presence and quantity of N_2H_4 above the liquid surface.

It would have been desirable in these runs to determine the N_2H_4 evaporation losses. The water losses were made up by adding about 200 ml H_2O every other day. Evaporation losses may have been significant due to the large volume of air (~61/min per tank) being bubbled continuously into the solution. The purpose in using the high volume of air was to preclude oxygen starvation during the oxidation stage.

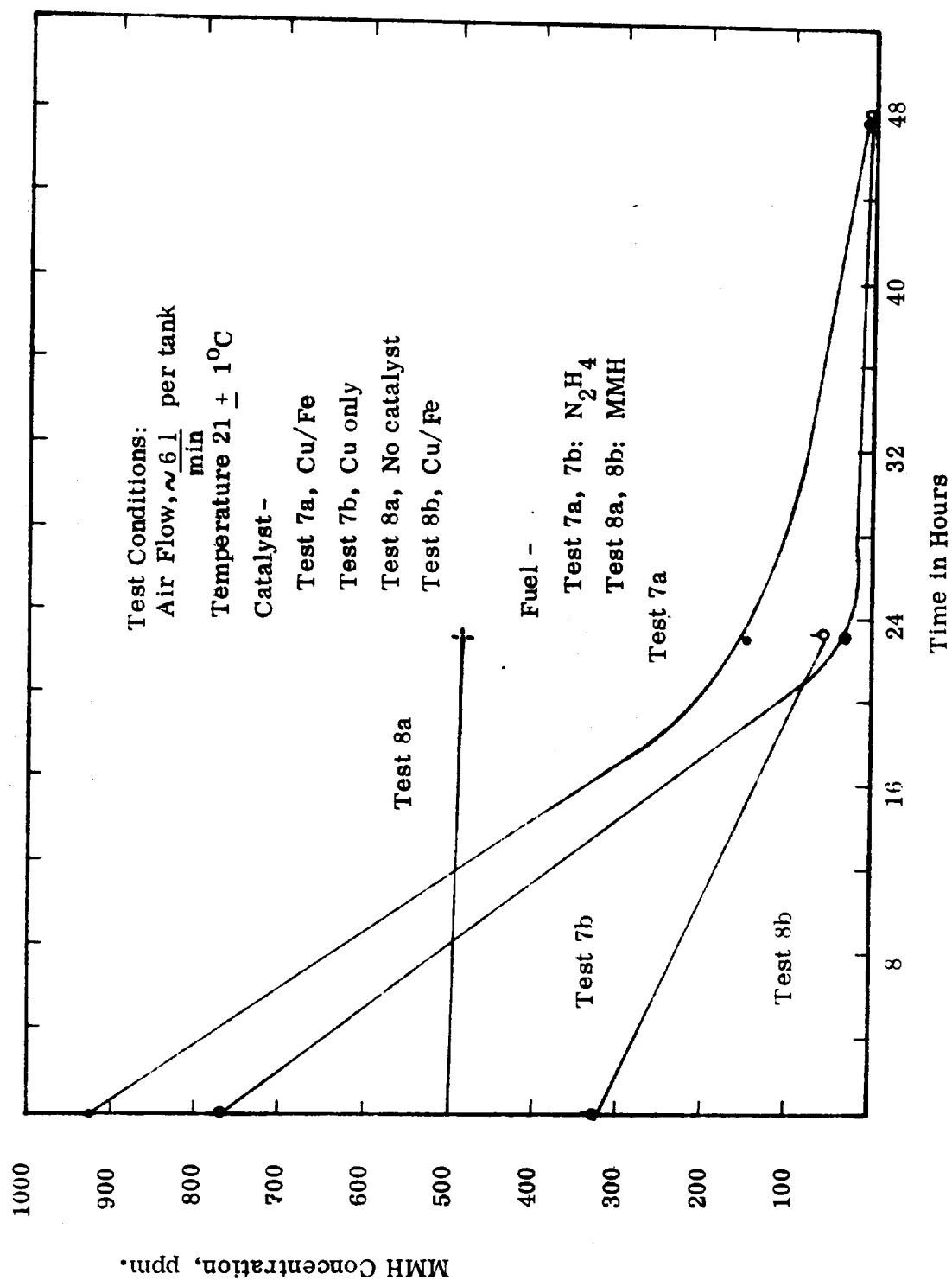


Figure 42. Air oxidation of N_2H_4 and MMH, Tests 7 and 8.

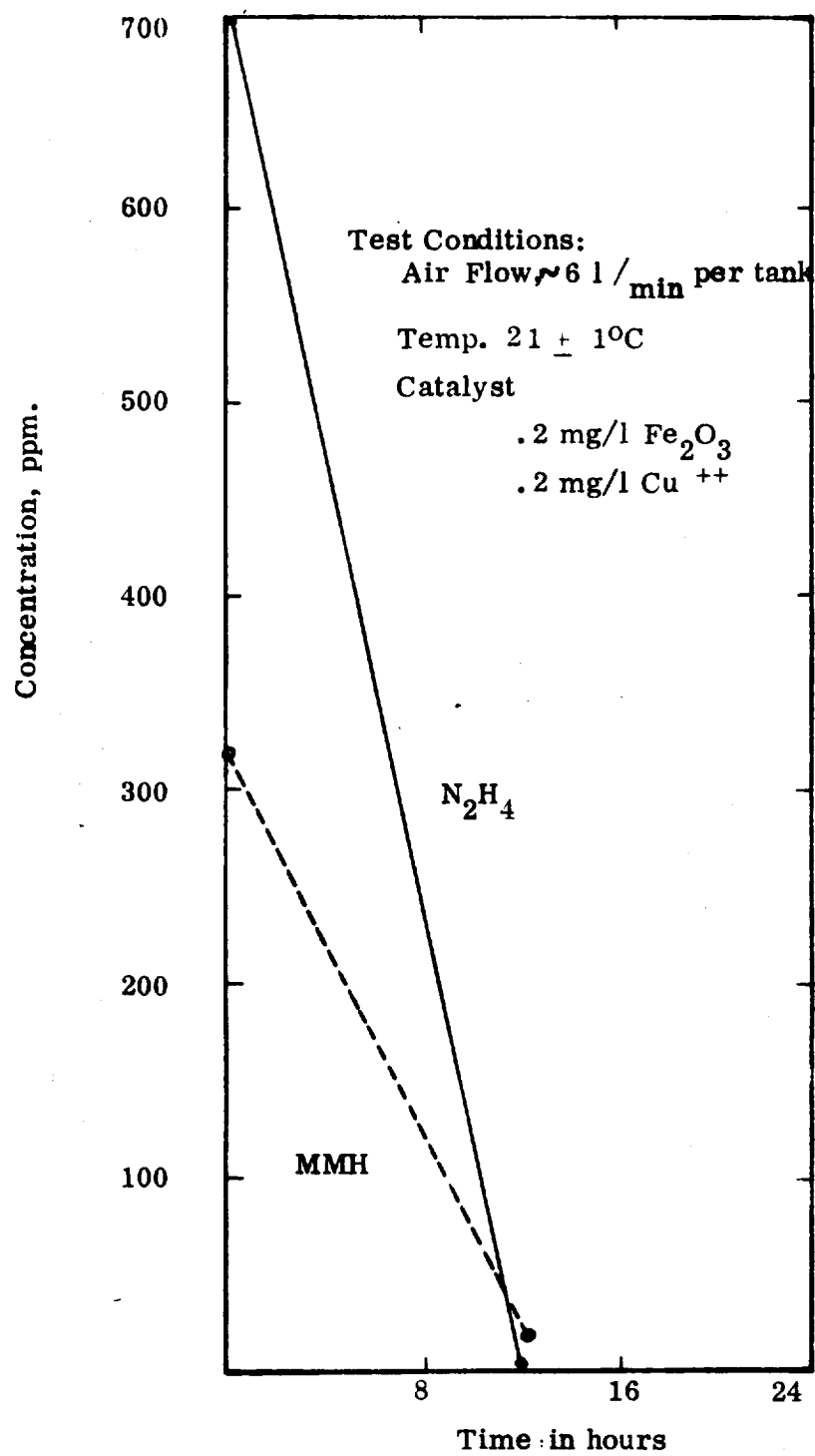


Figure 43. Air oxidation of N_2H_4 and MMH, Tests 9a and 9b.

The chlorine demand, which corresponds roughly to the amount of hydrazine in solution, was measured, with results in good agreement with the other measurements.

4. Conclusion

A catalytic - air bubbling method has been demonstrated for destruction of up to 900 ppm hydrazines within a total elapsed time of two days.

5. Recommendation

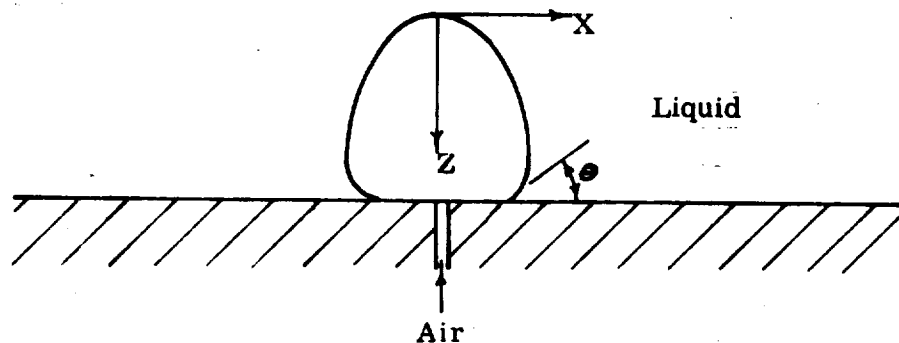
A comprehensive study of the catalytic - air bubbling method should be made to thoroughly investigate and obtain adequate cost figures, pollution data and operating procedures. Design parameters including aerator hole size and catalyst quantities should be optimized.

B. A DISCUSSION OF AIR BUBBLE GROWTH, DETACHMENT, AND RISE

1. Introduction

Engineering design considerations of aeration ponds must depend to a considerable extent on the size of bubbles formed. The purpose of this report is to present briefly the existing theories of bubble formation, growth, and detachment, and of the rise of small bubbles through bodies of liquid.

For simplicity, we will begin by considering the formation of a bubble resulting from the introduction of air (or other gas) very slowly through a single, isolated, small hole. "Small" will mean smaller than the base of the bubble at the instant of detachment. If the hole is located in a horizontal surface, a side view of the bubble will be somewhat as shown below:



The Z-axis is an axis of symmetry. The contact angle, θ , is defined as the angle between the solid boundary and the tangent to the bubble surface at its intersection with the solid boundary. The "base" refers to the portion of the bubble bounded by the solid surface rather than the liquid-vapor interface. In the case of static equilibrium, the bubble is subject to two external forces: the resultant of hydrostatic pressure on the water-air interface and air pressure on the base of the bubble, which is a buoyant-like force acting to remove the bubble from the surface; and the resultant of surface tension at the solid-liquid-gas intersection, acting to hold the bubble on the solid surface.

Simplified solutions based on assumptions regarding the bubble shape are tempting, but generally of little value and in fact simplified models are usually self-contradictory. One complication is the fact that Archimedes' Principle does not apply, since hydrostatic pressure does not act on all parts of the bubble surface. Therefore the relationship of base area to interface area and orientation, and the interrelationship of both with contact angle, is important. Considering that the liquid-gas interface in the vicinity of the solid surface becomes quite distorted just prior to detachment of the bubble, it is easy to understand why simplified models have not been successful in predicting the volumes of bubbles leaving solid boundaries.

This problem is an important one in boiling heat transfer, and at least in the static equilibrium case straightforward solutions exist, as discussed in the following section. In the case of aeration, considerations of bubble size are important in various ways.

1. The ratio of bubble surface area to volume is inversely proportional to diameter for similarly shaped bubbles, so that smaller bubbles have relatively more area for the air oxidation reaction to take place.
2. The air pressure in the bubble is inversely proportional to the curvature of the surface, and hence to diameter for similarly shaped bubbles, so that pumping requirements per unit volume of air in the pond are higher for smaller bubbles.
3. Assuming that the air always reaches pond temperature prior to leaving the aerator, the density of the air in the bubble is linearly proportional to the pressure, and hence inversely proportional to diameter, so that surface area per unit mass of air in the bubble is independent of size, and pumping requirements per unit mass of air or per unit surface area are higher for smaller bubbles (even more so if the smaller orifices required for the smaller bubbles are taken into consideration.)
4. Smaller bubbles rise more slowly through the pond, as discussed in a later section, and hence there is more time for the reaction to take place.
5. On the other hand, both the faster motion and larger size of larger bubbles help generate circulation in the pond, bringing the contents of the pond into contact with the air bubbles sooner and more frequently.

It therefore seems apparent that there is no obvious, easy answer to the question of best bubble size. A careful, detailed optimization would have to be

performed, in terms of pond depth and other pond parameters. An exception would be a case where the bubbles contain N_2O_4 or other toxic vapors, so that the only important consideration would be complete reaction prior to the bubble reaching the pond surface, and the choice of the smallest feasible bubble size is clearcut.

2. Analysis

The preceding section discussed the need for applying force equilibrium considerations at all points of the bubble surface, rather than trying to assume a shape and apply an overall force balance. Performing a force balance on a surface element results in the capillary equation¹

$$\frac{1}{R} + \frac{\sin \phi}{X} = \frac{2}{b} - \frac{g(\rho_2 - \rho_1)}{\sigma} Z \quad (1)$$

where

X, Z are coordinates as shown in the sketch of the preceding section

R, $\frac{X}{\sin \phi}$ are principal radii of curvature, R in a plane containing the axis of symmetry

ϕ is the angle which the perpendicular from the interface makes with the axis of symmetry, measured from the apex ($\phi = 0$ at $X = 0, Z = 0$)

b is the radius of curvature at the apex (origin)

ρ_1, ρ_2 are the densities of the gas and liquid, respectively

σ is the surface tension at the interface

g is the gravitational acceleration

This equation has been treated by many authors, with most modern work patterned more or less after the work of Bashforth and Adams, whose book² reported the results of numerical calculations dating from 1855 (all by hand, supported by a 50 pound grant from the Royal Society).

¹A detailed derivation, including more generality regarding orientation of the solid surface relative to gravity, has been presented by B. K. Larkin, "Numerical Solution of the Equation of Capillarity," Journal of Colloid and Interface Science, Vol. 23, pp. 305-312 (1967).

²Bashforth, F. and J. C. Adams, An Attempt to Test the Theories of Capillary Action. University Press, Cambridge, England, 1883.

This work is also believed to be the first application of Adams' predictor - corrector method, a numerical technique that is still useful for certain types of problems. In essence, their work amounted to starting at the origin and numerically calculating the shape of a surface for a given value of b and the dimensionless constant

$$\beta \equiv \frac{g(\rho_2 - \rho_1)}{\sigma} b^2$$

The results were families of possible surface shapes for each value of β considered. Boundary conditions would be applied by truncating a curve at a point where its slope corresponds to the desired contact angle.

These results were applied by Wark³ to the specific calculation of sizes and shapes of air bubbles in water at 20°C. Of even more interest for our application is the work of Fritz⁴, who developed a technique for using the Bashforth and Adams results to find the maximum (detachment) sizes of bubbles as a function of contact angle and capillary constant. Fritz's results are reproduced directly in Figures 44 and 45 below. In Figure 44, the capillary constant is

$$a \equiv \sqrt{\frac{2\sigma}{(\rho_2 - \rho_1)g}}$$

and in Figure 45, Curve 1 is the case of primary interest here, air bubbles in water at 20°C.

³Wark, I. W., "The Physical Chemistry of Flotation. I: The Significance of Contact Angle in Flotation." Vol. 37, p. 623 - 644, (1933).

⁴Fritz, W., "Berechnung des Maximalvolumens von Dampfblasen" ("Calculation of the Maximum Volumes of Vapor Bubbles"). Physik. Zeitschr., Vol. 36, pp. 379-384 (1935).

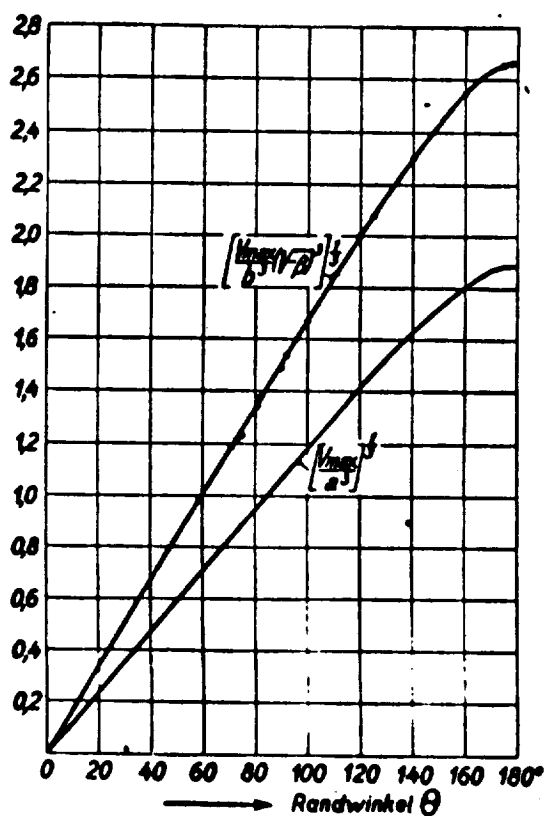


Abb. 4. Dimensionslose Darstellung des Maximalvolumens V_{\max} in Abhängigkeit vom Randwinkel.

Figure 44. Fritz's dimensionless presentation of the maximum volume V_{\max} as a function of contact angle.

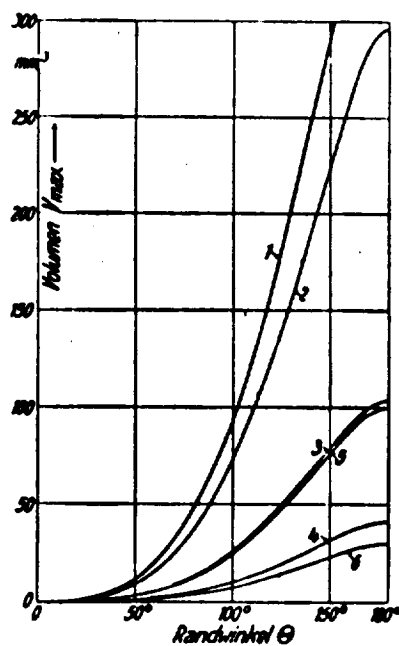


Abb. 6. Maximalvolumen von verschiedenen Gas- und Dampfblasen. Kurve 1: Luftblase in Wasser von 20° C; 2: Wasser-Dampfblase 1,03 kg/cm²; 3: Wasser-Dampfblase 50 kg/cm²; 4: Wasser-Dampfblase 100 kg/cm²; 5: Quecksilber-Dampfblase 1,03 kg/cm²; 6: Tetrachlorkohlenstoff-Dampfblase 1,03 kg/cm².

Figure 45. Maximum volumes of various gas and vapor bubbles, from Fritz.

Modern investigators have used the digital computer to extend Fritz's results to other cases, and in the process have verified the validity of the Fritz and Bashforth and Adams calculations. In particular, Larkin⁵ has developed a method of solution for nonaxisymmetric surfaces and gravitational accelerations that are arbitrary in both direction and magnitude, and Concus⁶ has described liquid - gas interfaces in right circular cylinders. This last case might be applicable in the case of aerators with larger orifice sizes, since the interface inside the circular orifice might be of primary interest.

3. Discussion

The results above show that small bubbles result from small values of either surface tension or contact angle - given of course, the essential prerequisite of a small pore size relative to the size of the bubbles being formed. Surface tension is a temperature-dependent property of the water-air system, but surface tension modifiers-detergents, for example - are readily available for water. The effect of these "surfactants" is to reduce the surface tension. Their effect on newly forming surfaces is unknown, however, at least to the present author. Contact angles, on the other hand, can be varied over a wide range.

The contact angle is a temperature-dependent property of a solid-liquid-gas system. Current knowledge of contact angles is due, in large part, to the work of William A. Zisman and various coworkers over a period of many years. Their results were summarized by Zisman⁷ in 1964. One simple

⁵Op. cit. See also McGrew, J. L., and B. K. Larkin, "Cryogenic Liquid Experiments in Orbit, Vol. II: Bubble Mechanics, Boiling Heat Transfer, and Propellant Tank Venting in a Zero-Gravity Environment." NASA CR-652, December 1966.

⁶Concus, P., "Static Menisci in a Vertical Right Circular Cylinder." J. Fluid Mech., Vol. 34, pp. 481-495 (1968).

⁷Zisman, W. A., "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution, in Contact Angle, Wettability and Adhesion." Advances in Chemistry Series 43, R. F. Gould (Ed.), American Chemical Society Applied Publications, 1964, p. 1.

expression for contact angle that resulted from this work has proven useful in a great many cases:

$$\cos \theta = 1 - k (\sigma_L - \sigma_c), \quad (3)$$

where k and σ_c are empirical constants, σ_c being named the "critical surface tension" of the solid surface by Zisman. σ_L is the actual surface tension of the liquid-gas interface. If $\sigma_L < \sigma_c$, the contact angle is near zero, (There is some question whether a true zero contact angle can exist.) Solid surfaces are characterized as being "high energy" or "low energy" according to whether their critical surface tension values are high or low, respectively. In general, metals are high energy surfaces, while the lowest values of σ_c are associated with highly fluorinated organic polymers and other organic compounds made up largely of CF_2 and CF_3 groups.

To achieve small values of θ , then, it is apparent that metallic surfaces with large values of σ_c are desirable. In the case of water, however, there is a particular problem that has been noticed by most researchers concerned with liquid surface phenomena.

Because of the unusually high surface tension of water, the contact angle between a water - air interface and a metal surface fluctuates over a wide range, as indicated by equation (3) when the term in brackets becomes the difference between two large numbers. An additional aspect of this problem is discussed by Frohnsdorff and Tejada⁸ in the following terms:

"The measurement of the true contact angles of high surface tension liquids such as water on high energy surfaces such as metals is difficult because of the strong tendency of the metals to adsorb organic vapors. Even a small fraction of a monolayer of organic molecules appears to be sufficient to increase the contact angle of water on many surfaces..."

Perhaps the first extensive treatment of this problem was that of Trevoy and Johnson⁹ in 1958. It became very much a problem in connection with the zero-gravity experimentation of the early 1960's carried out in support of

⁸Frohnsdorff, G., and S. B. Tejada, "Measurement of Contact Angles and Evaluation of Surface Coatings." Final Report, Contract NAS3-13725, NASA Lewis Research Center. NASA CR 72975, August 1971.

⁹Trevoy, D. J., and H. Johnson, Jr., "The Water Wettability of Metal Surfaces." J. Phys. Chem., Vol. 62, p. 833 (1958).

spacecraft propellant tank design efforts, and as a result the Lewis Research Center funded an extensive evaluation of procedures for cleaning metal surfaces to obtain "true" contact angles in laboratory work¹⁰. The conclusion was that the best procedure was vapor degreasing followed by immersion in an alkaline cleaner and thorough rinsing with water.

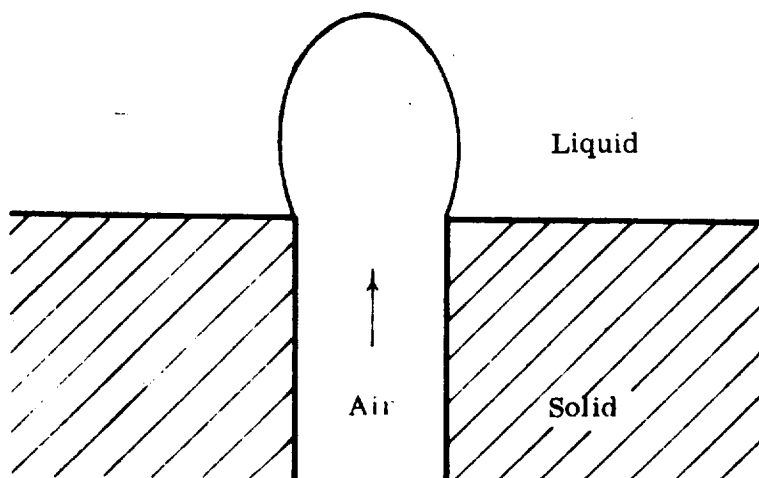
For cooling pond applications where small bubbles are desired, it seems likely that some benefit could be derived from using metal pipes for the actual aerator, degreasing them prior to installation, insuring that they remain submerged in a somewhat alkaline pond, and installing an oil trap on the compressed air line. For the sake of computation, however, it is probably best to assume the worst, which is probably a contact angle on the order of 80° to 100° . Contact angles reported by Frohnsdorff and Tejada for water at 20°C on cleaned and polished metal surfaces range from 8° to 12° for copper and aluminum surfaces, 16° to 20° for stainless steel.

4. Larger Orifice Sizes

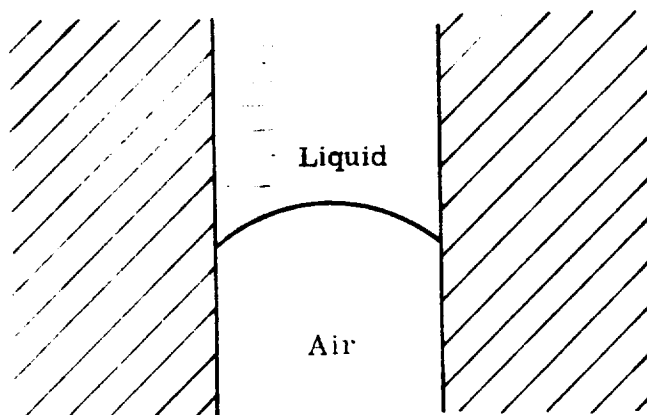
One assumption in our discussion thus far has been an aerator orifice size much smaller than the bubble size. Curve 1 of Figure 45 shows that, at $\Theta = 100^\circ$, the maximum volume is about 90 mm^3 , corresponding to a sphere of 5.5 mm diameter. Hence this size bubble would not be expected to emanate from orifices larger than about this size. In the case of smaller contact angles, the restriction on hole size would be more severe.

If we consider the air hole to be sharp-cornered as shown in the sketch below, the contact angle ceases to be the controlling boundary condition if the interface is attached to the edges of the hole. Rather, the hole diameter predominates. A meaningful analysis would probably have to follow an approach similar to Fritz's, seeking in this case the largest member of the family of curves that can be spanned by the orifice diameter, rather than the largest member that will allow the requisite contact angle to be realized. (Note that the interface remains attached to the corner as its orientation changes through 90° , for constant contact angle.)

¹⁰ Schwartz, A. M. and A. H. Ellison, "The Effect of Surface Contamination on Contact Angles and Surface Potentials." NASA CR 54708, 1966.



Without attempting to actually solve the problem, we may surmise the following. If the hole is considerably smaller than the maximum bubble diameter as calculated by Fritz, the bubble will reach the top of the hole, grow for a period while attached to the corner, and then spread across the horizontal surface as shown in the sketch at the beginning of this report. For increasingly larger hole sizes, a point is reached for which the bubble grows to Fritz's maximum volume while attached to the corner, and hence cannot spread across the horizontal surface but detaches instead. For still larger holes, the bubble probably grows on the corner to a value somewhat greater than Fritz's maximum volume and detaches. As hole size increases, however, a point is reached for which a stable interface inside the hole is impossible.



This last case is entirely analogous to the well-known experiment in which water is picked up in a soda straw closed at the top by one's finger. The water in the straw is supported by air pressure, but only because the lower air-water interface is stable. The experiment cannot be repeated with a larger diameter tube, even though air pressure is equally capable of supporting the water, because of instability of the lower interface. It is also entirely analogous to the problem of liquid propellants in cylindrical tanks under low-gravity conditions, and hence the solution is by now well-known, and experimental verification is abundant.

The first comprehensive analysis was that of Reynolds, Satterlee, and Saad^{11, 12, 13}, results of which are presented in Figure 46. The dimensionless parameter $\rho g R^2 / \sigma$ is known as the Bond number; ρ replaces the $(\rho_2 - \rho_1)$ density difference of earlier pages since $\rho_1 \ll \rho_2$ in most cases of interest. The critical Bond number for $\theta = 100^\circ$ is 3.33, giving a critical diameter of 10.0 mm, compared to Fritz's maximum bubble volume of 90 mm³. The difference is more striking at smaller contact angles. At 50° , Fig. 45 gives a maximum volume of 11.7 mm³, corresponding to a sphere of 2.8 mm diameter; the critical Bond number from Figure 46 is 2.73, giving a critical hole diameter of 9.0 mm.

The conclusion is that these larger holes will produce larger bubbles up to the point where the hole diameter reaches the critical value calculated from the data of Figure 46. For holes larger than this critical size, the aerator will presumably produce bubbles whose size is governed by other factors besides hole size - flow rate and tube dimensions, for example - with a good likelihood that bubbles smaller than the opening size will be produced.

¹¹Satterlee, H. M. and W. C. Reynolds, "The Dynamics of the Free Liquid Surface in Cylindrical Containers Under Strong Capillary and Weak Gravity Conditions." Tech. Rept. No. LG-2, Dept. of Mech. Eng., Stanford Univ., May 1964.

¹²Reynolds, W. C., M. A. Saad and H. M. Satterlee, "Capillary Hydrostatics and Hydrodynamics at Low-g." Tech. Rept. No. LG-3, Dept. of Mech. Eng., Stanford Univ., May 1964.

¹³Reynolds, W. C. and H. M. Satterlee, "Liquid Propellant Behavior at Low and Zero g." Chap. 11 in The Dynamic Behavior of Liquids in Moving Containers, H. N. Abramson, ed., NASA SP-106, 1966.

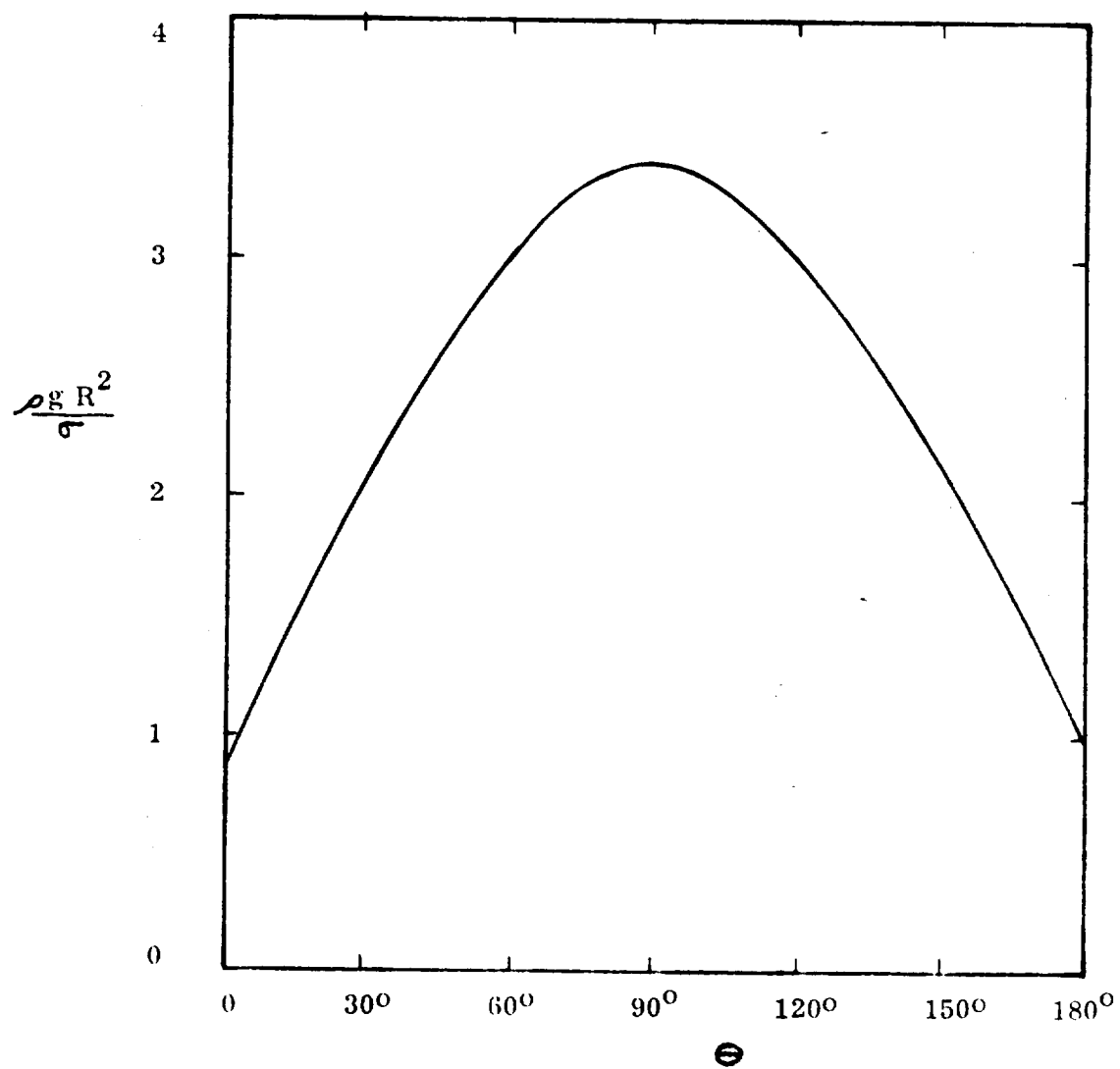


Figure 46. Stability limit for an inverted meniscus in a cylindrical tube.

5. Dynamic Effects

So far, we have assumed that static equilibrium conditions prevail at the time of bubble detachment. If the bubble grows rapidly, dynamic effects can be important in three ways.

1. If the bubbles leave the aerator as a closely-spaced stream, due to rapid growth and detachment, they generate liquid motion away from the aerator in the vicinity of the bubble source. This liquid motion then tends to sweep newly-formed bubbles off the aerator surface before they reach their static equilibrium maximum volume.
2. The growth of the bubble itself might generate liquid motion away from the wall. If the volume changes linearly with time, then the linear dimensions of the bubble change rapidly at first, more slowly as time goes on. Therefore in the early stages of bubble growth, the rapid motion of its top surface away from the wall can generate liquid motion that then tends to drag the slowly growing bubble in a later stage of development off the wall.
3. Contact angle in the dynamic case is known to be a function of the velocity of the contact line, and also differs depending on whether the contact line is moving toward (advancing) or away from (receding) the gas phase - a phenomenon known as contact angle hysteresis. Investigations of dynamic contact angles to date have all been concerned with advancing contact angles, as far as we know, whereas the receding contact angle is the important one in the case of a growing bubble. The velocity dependence was demonstrated experimentally in 1962 by Rose and Heinz¹⁴, who considered flow over a dry surface. The problem was then taken up by Friz¹⁵, who analyzed the advance of a liquid over a previously-wetted surface. The numerical results led to the conclusion that contact angle depends on contact line velocity U_0 according to

$$\tan \theta = 3.4 \left(\frac{U_0 \mu}{\sigma} \right)^{1/3}$$

¹⁴Rose, W. and R. W. Heinz, "Moving Interfaces and Contact Angle Rate-Dependency." J. Colloid Sci., Vol. 17, pp. 39-48 (1962)

¹⁵Friz, G., "Über den dynamischen Randwinkel im Fall der vollständigen Benetzung." Zeit für angew. Physik, Vol. 19, pp. 374-378 (1965).

μ being the viscosity. Ellison and Tejada¹⁶ performed a series of experiments in which liquid advanced over a dry surface, and concluded that in this case the data could be correlated by the relation

$$\theta = A \tanh(CU_0) + D U_0^{1/3},$$

A, C, and D being empirical coefficients. The Friz equation was found to give poor agreement with their results because of the difference in initial conditions. A set of experiments in which the situation analyzed by Friz was carefully reproduced was carried out by Coney and Masica¹⁷, who concluded that the Friz equation "is adequate." The results are shown in Figure 47; the slight trend toward higher contact angles than predicted was thought to result from experimental error.

In summary, it appears that dynamic effects will result in smaller bubbles than predicted by static equilibrium considerations, except possibly for a dynamic contact angle effect in the case of rapidly growing bubbles. Even here, it is likely that just as advancing contact angles increase with velocity, receding contact angles should decrease with velocity, which would also result in smaller bubbles leaving the aerator.

6. Other Effects

In summary, we first considered the static equilibrium of a bubble assuming the hole to be too small to be a consideration, then looked at the effects of larger holes, defining essentially three regimes - hole too small to be significant, hole-dominated, and hole too large to be significant - and finally proceeded to consideration of dynamic effects. Of the other effects that might be important, the most significant is the proximity of other bubble sources, since we have always considered bubbles emanating from single, isolated sources.

Other nearby bubble sources can have at least two effects. By adding to the vertical fluid motion in the vicinity of the aerator, they tend to reduce the bubble size still more as bubbles are pulled away from the surface before

¹⁶ Ellison, A. H. and S. B. Tejada, "Dynamic Liquid/Solid Contact Angles and Films on Contaminated Mercury." NASA CR 72441, July 1968.

¹⁷ Coney, T. A. and W. J. Masica, "Effect of Flow Rate on the Dynamic Contact Angle for Wetting Liquids." NASA TN D-5115, March 1969.

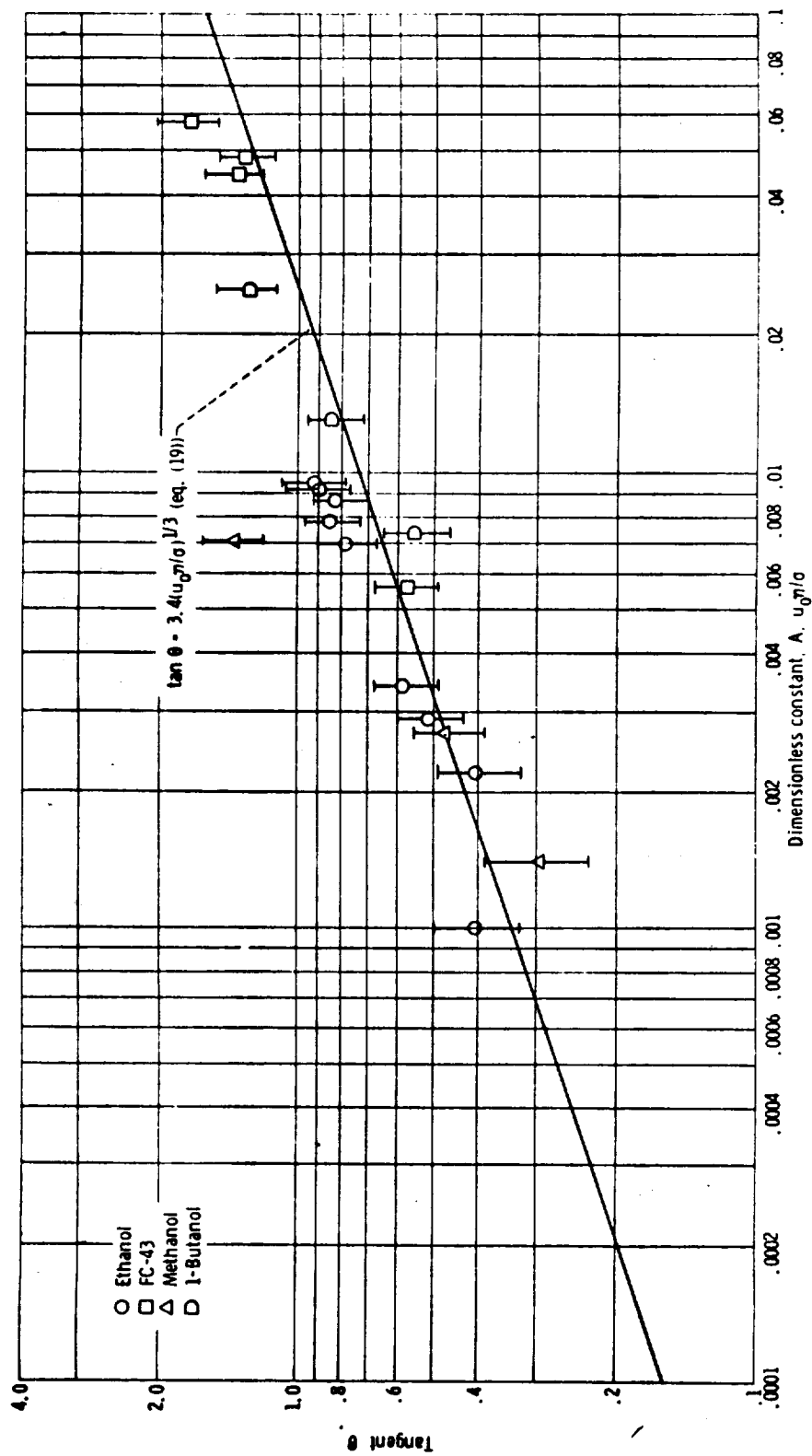


Figure 47. Coney and Masica's experimental results for dynamic contact angle, compared to Friz's equation. Reproduced from NASA TN D-5115.

reaching their static equilibrium maximum size. On the other hand, if the sources are very close there is a possibility of bubble coalescence, resulting in larger bubbles than predicted.

The potential energy associated with the surface of a free bubble is σA , the product of surface tension and surface area. If two spherical bubbles, each of radius R_1 , coalesce to form one bubble of radius R_2 , conservation of mass for the air within the bubble requires

$$2 \rho_1 R_1^3 = \rho_2 R_2^3$$

and, if we assume the process to be isothermal, the ratio of densities will equal the ratio of pressures,

$$\frac{\rho_2}{\rho_1} = \frac{p_2}{p_1} = \frac{p_a + 2\sigma/R_2}{p_a + 2\sigma/R_1}$$

yielding

$$R_2 = R_1 \left(2 \frac{p_a + 2\sigma/R_1}{p_a + 2\sigma/R_2} \right)^{1/3}$$

The limiting cases, $(p_a R_1 / \sigma) \rightarrow 0$ and $(p_a R_2 / \sigma) \rightarrow \infty$ yield the result

$$2^{1/3} R_1 \leq R_2 \leq 2^{1/2} R_1$$

and hence if we compare the initial and final potential energies,

$$P.E._1 = 2(4\pi R_1^2)\sigma, \quad P.E._2 = 4\pi R_2^2\sigma,$$

the result is

$$2^{-1/3} \leq \frac{P.E._2}{P.E._1} \leq 1$$

The conclusion is two-fold. First, two bubbles that come into contact with each other will always tend to coalesce because of the resultant decrease in potential energy. Second, the resultant bubble will be at least twice the volume of each original bubble, and perhaps as large as $2^{3/2} = 2.83$ times the volume of each original bubble.

7. Bubble Rise Velocities

Once the bubble detaches from the aerator surface it rises through the pond at a velocity dependent on the size of the bubble. The study of bubble rise velocities was especially active in the 1950's, with particularly significant papers being those of Haberman and Morton¹⁸ (experimental) and Moore¹⁹ (theoretical).

Bubble rise velocity was found to depend on Reynolds and Weber numbers,

$$R = 2r_e U \rho / \sigma$$

$$W = 2r_e U^2 \rho / \sigma$$

and also on a third dimensionless parameter, M, defined as

$$M = g \mu^4 / \rho \sigma^3 ,$$

where

$$r_e = \text{equivalent bubble radius, } r_e = (3V/4\pi)^{1/3}$$

U = terminal velocity

ρ = liquid density

μ = liquid viscosity

σ = surface tension

g = gravitational acceleration

A quote from Moore will serve to summarize the Haberman and Morton results very concisely:

"For low M liquids ($M < 10^{-8}$) the terminal velocity at first increases rapidly as r_e increases, achieves a maximum and after falling to a minimum rises gradually again. For high M liquids ($M > 10^{-3}$), the terminal velocity increases steadily with r_e , though the rate of increase falls off at a fairly well defined value of r_e .

¹⁸Haberman, W. L. and R. K. Morton, David Taylor Model Basin Rept. No. 802, 1953.

¹⁹Moore, D. W., "The Rise of a Gas Bubble in a Viscous Liquid." J. Fluid Mech., Vol 6, pp. 113-130 (1959).

"For low M liquids the shape is at first spherical, then increasingly oblate, then, at about the radius corresponding to the maximum velocity, the shape fluctuates rapidly about an oblate form until, for very large values of r_c , the bubbles attain a striking umbrella shape which is quite steady at its frontal surface though the rear of the bubble fluctuates. These spherical cap bubbles were the subject of an important investigation by Davies and Taylor²⁰ (1950). For high M liquids the spherical cap shape is achieved without the bubble surface ever becoming unsteady.

"For low M liquids the bubble trajectory is at first rectilinear, then, at about the bubble radius for maximum terminal velocity, both planar zig-zag and spiral trajectories are observed. Finally, the spherical cap bubbles rise in very nearly linear trajectories. For low (sic) M liquids only rectilinear trajectories are observed."²¹

Figures 48 & 49 show the Haberman and Morton results in terms of the drag coefficient of the bubbles as a function of Reynolds and Weber numbers, with M as a parameter. The expression for terminal velocity in terms of drag coefficient is

$$U = \sqrt{\frac{8r_c g}{3 C_D}}$$

Use of this information to find terminal velocity is of course complicated by the fact that R and W are defined in terms of this velocity. The present author can only quote without comment Moore's statement that "it is more illuminating to consider the drag coefficient C_D rather than U ..."

These results show the Reynolds number variation is independent of M except in the range $10 < R < 10^3$, whereas the Weber number dependence varies greatly with M in terms of the location, but not shape or slope (in the log-log plot) of the curves.

Moore's analysis produced the significant result that the drag coefficient for a spherical bubble is given by

$$C_D = 32/R,$$

²⁰ Davies, R. M. and G. I. Taylor, "The Mechanics of Large Bubbles Rising through Extended Liquids and through Liquids in Tubes." Proc. Roy. Soc. A, Vol 200, pp.375-390 (1950).

²¹ Moore, D. W., op. cit.

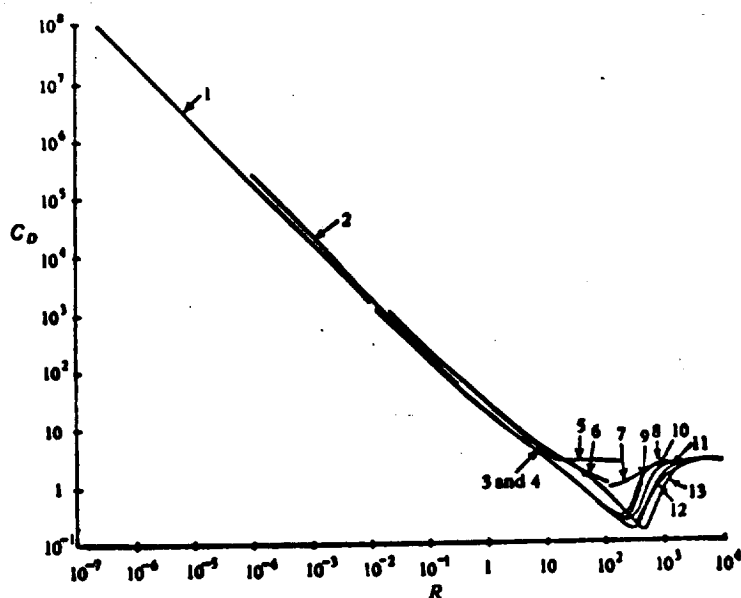


FIGURE 1. The drag coefficient as a function of the Reynolds number (reproduced from Haberman & Morton 1953).

1. Syrup (Bond), $M = 0.92 \times 10^6$.
2. Olive oil (Arnold), $M = 0.716 \times 10^{-2}$.
3. Water + 62 % corn syrup, $M = 0.155 \times 10^{-2}$.
4. Water + 68 % corn syrup, $M = 0.212 \times 10^{-2}$.
5. Mineral oil, $M = 1.45 \times 10^{-2}$.
6. Water + 56 % glycerine (Bryn), $M = 1.75 \times 10^{-7}$.
7. Water + 42 % glycerine (Bryn), $M = 4.18 \times 10^{-2}$.
8. Turpentine, $M = 24.1 \times 10^{-10}$.
9. Water + 13 % ethyl alcohol (Bryn), $M = 1.17 \times 10^{-2}$.
10. Varsol, $M = 4.3 \times 10^{-10}$.
11. Cold water (filtered), $M = 1.08 \times 10^{-10}$.
12. Methyl alcohol, $M = 0.89 \times 10^{-10}$.
13. Water (filtered), $M = 0.26 \times 10^{-10}$.

Figure 48. Moore's presentation of the Haberman and Morton results: Reynolds number dependence.

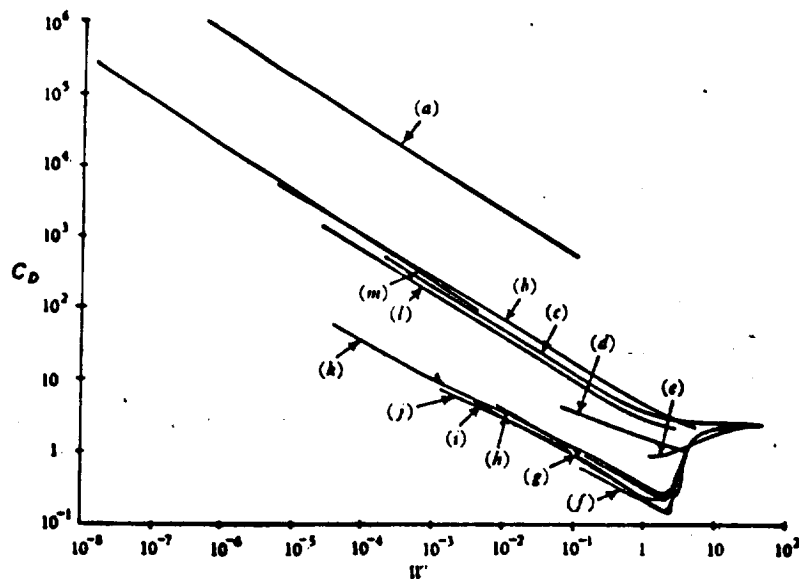


FIGURE 2. The drag coefficient as a function of the Weber number (reproduced from Haberman & Morton 1953).

- (a) Syrup (Bond), $M = 0.92 \times 10^4$.
- (b) Water + 68 % corn syrup, $M = 0.212 \times 10^{-3}$.
- (c) Mineral oil, $M = 1.45 \times 10^{-3}$.
- (d) Water + 56 % glycerine (Bryn), $M = 1.75 \times 10^{-3}$.
- (e) Water + 42 % glycerine (Bryn), $M = 4.18 \times 10^{-3}$.
- (f) Methyl alcohol, $M = 0.89 \times 10^{-10}$.
- (g) Water + 13 % ethyl alcohol, $M = 1.17 \times 10^{-3}$.
- (h) Turpentine, $M = 24.1 \times 10^{-10}$.
- (i) Varsol, $M = 4.3 \times 10^{-10}$.
- (j) Water (filtered), $M = 0.26 \times 10^{-10}$.
- (k) Cold water, $M = 1.08 \times 10^{-10}$.
- (l) Water + 62 % corn syrup, $M = 0.155 \times 10^{-3}$.
- (m) Olive oil (Arnold), $M = 0.716 \times 10^{-3}$.

Figure 49. Moore's presentation of the Haberman and Morton results: Weber number dependence.

subject to the restrictions that R is large and W small, and showed that both conditions can be satisfied in low M liquids. Comparison with the experimental results showed good agreement except for a slight displacement of the theoretical curve below experimental values.

Extension of the theory to non-spherical bubbles was also treated by Moore, but the results were less conclusive and are felt to be beyond the scope of the present discussion.

The expression $C_D = 32/R$ can be solved for U, giving

$$U = \frac{\rho g r_e^2}{6\mu}$$

which gives, for water at 20°C,

$$U = 1.63 r_e^2 \text{ meters/second,}$$

if r_e is in mm.

IV. SCRUBBERS

1. Flow Rates and Sizing of Scrubbers

The performance of a gas scrubbing operation involving only solution of a contaminant with no chemical reaction is limited by the equilibrium relation between the contaminated gas and the contaminated scrubbing liquid.

For scrubbing gases, the operating lines and initial and final points are constrained to lie on the side of the equilibrium line on which the contaminant concentration in the gas is greater than equilibrium concentration at any given concentration of contaminant in liquid. The slope of the operating line on a gas phase concentration vs. liquid phase concentration curve is given by the ratio of liquid flow rate (moles/area/time) to gas flow rate. Thus if the equilibrium curve is known, and the flow rate and degree of contamination of the entering gas is known, and the permissible degree of contamination of the leaving gas is given, the minimum liquid flow rate (liquid flow rate for an infinitely long scrubber) can be found¹.

The foregoing obtains for cocurrent as well as countercurrent flow-scrubbers, though we are here primarily concerned with the latter. The schematic diagram (Figure 50) shows an example of an equilibrium curve and an operating curve for a countercurrent scrubber. Crudely speaking, the length of a scrubber is inversely proportional to the distance between the equilibrium and operating lines. It is conventional that the equilibrium and operating lines be approximately parallel, as the equilibrium line permits. With the equilibrium line known, the gas flow rate and gas initial contamination concentration also known, and with the outlet gas contamination specified, the operating line for an infinitely long scrubber will be the straight line passing through the specified concentration points, tangent at one or more points to the equilibrium line, and elsewhere above the equilibrium line. Since the operating line and the gas flow rate are known, and the line's slope is the ratio of liquid and gas flow rates, the minimum liquid flow rate is determined. For a finite-length scrubber, the liquid flow rate is necessarily greater than for an infinitely long scrubber.

¹Calvert, Seymour, "Source Control by Liquid Scrubbing." Ch. 46 in AIR POLLUTION, Vol. III, ed. by Arthur Stern, Academic Press, New York, 1968.

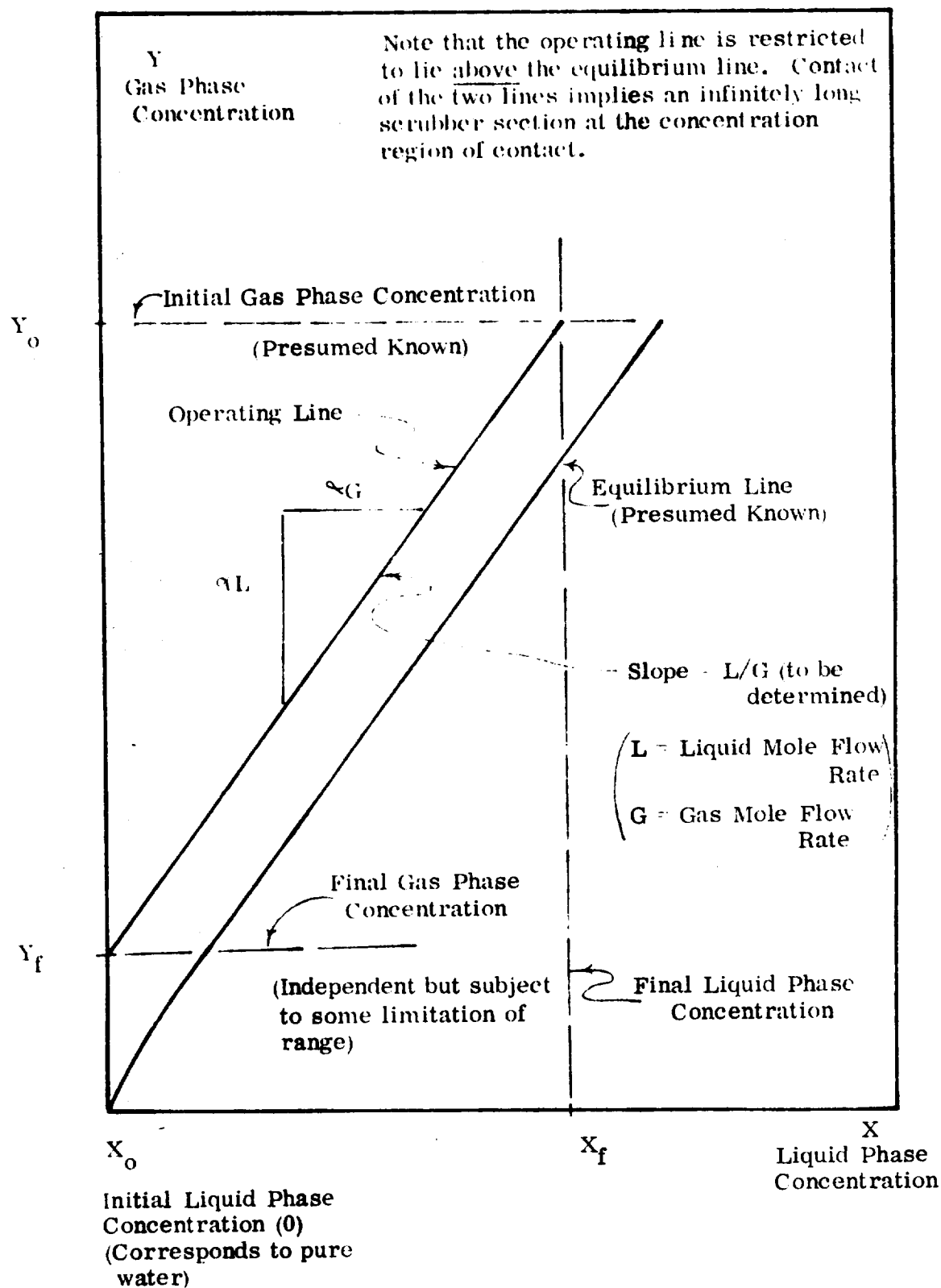


Figure 50. Typical scrubber performance chart.

Equilibrium curves for air and water contaminated with N_2H_4 , CH_3NHNH_2 (MMH) and NO_2 , at room temperature, are presented in Figure 51.

The concentration of noxious gases immediately over a solution is proportional to the vapor pressure of the liquid. The vapor pressure can be estimated from Raoult's law which states that the partial vapor pressure of any constituent of a solution is equal to the vapor pressure of the pure substance multiplied by the mole fraction of that constituent in solution. Figures 52, 53 and 54 show the partial pressures in air for mixtures of the various propellants with water as calculated using Raoult's law, and also the vapor pressure for the solution. (This latter function varies linearly from the vapor pressure of pure water, on the left side, to the vapor pressure of pure propellant on the right side.)

Once the vapor pressure is calculated, the number of moles of each gas per liter can be approximated by the ideal gas law. (1 atm at 25°C was chosen). The weights of the gases are calculated and the weight concentrations can be found. The concentration of the vapor in air is a function of the concentration of the contaminant in water.

For HNO_3 ,

wt conc in air $\approx .05$ (wt conc in water), wt conc in water $< .1$

For MMH,

wt conc in air $\approx .01$ (wt conc in water), wt conc in water $< .1$

For N_2H_4 ,

wt conc in air $\approx .025$ (wt conc in water), wt conc in water $< .1$

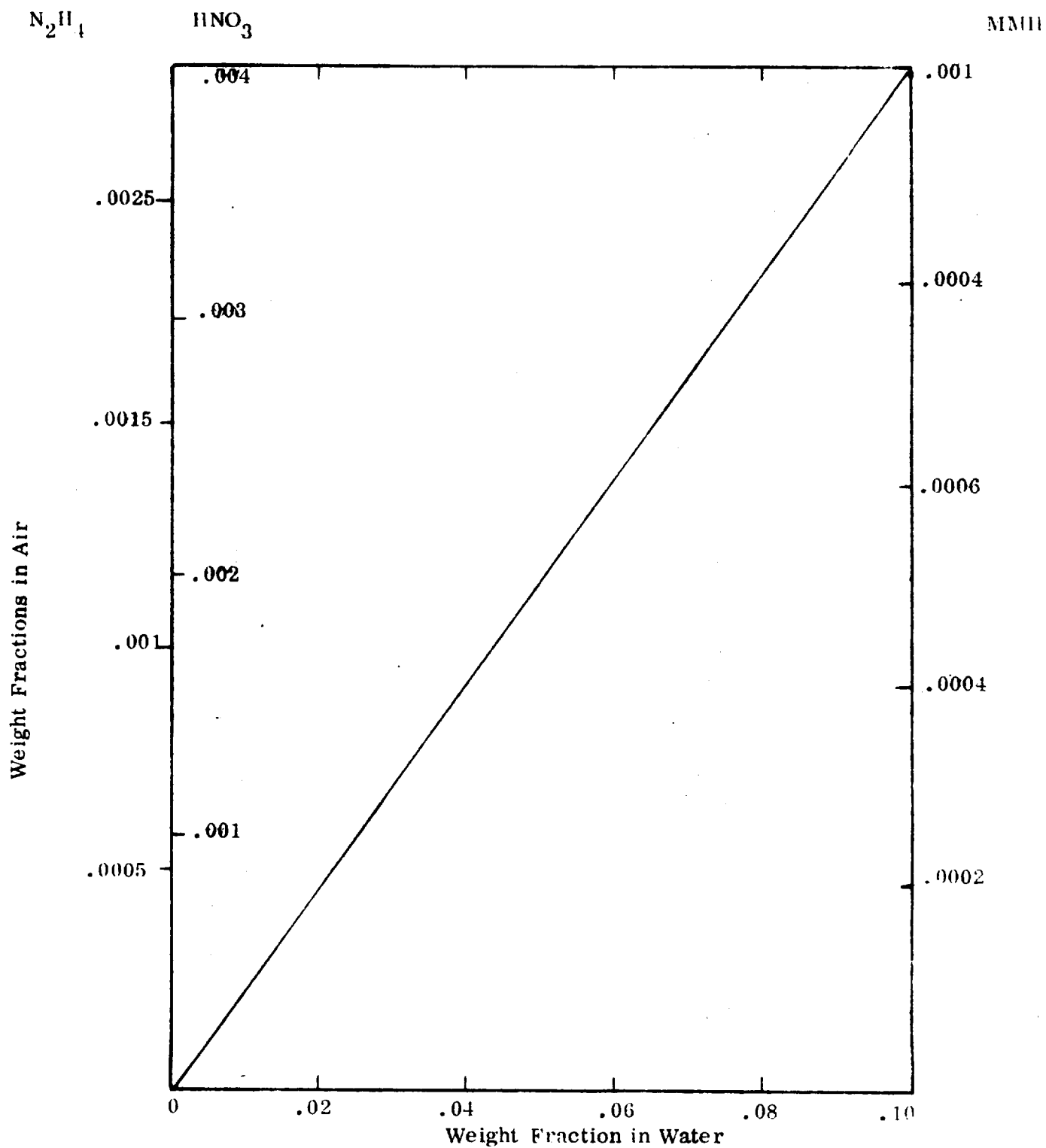


Figure 51. Equilibrium curves for hypergolic propellants in air and water.

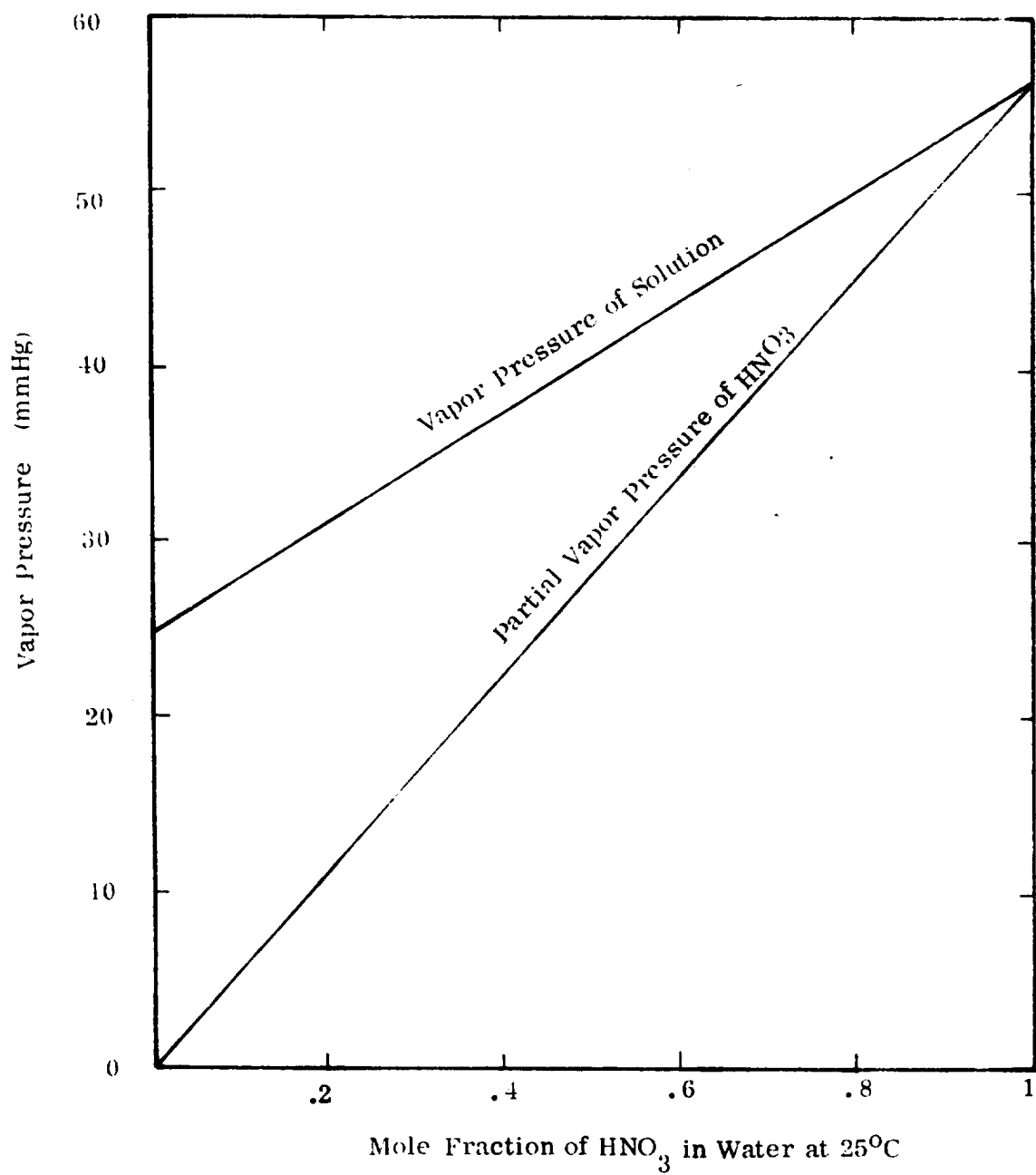


Figure 52. Vapor pressures of HNO₃/H₂O mixtures

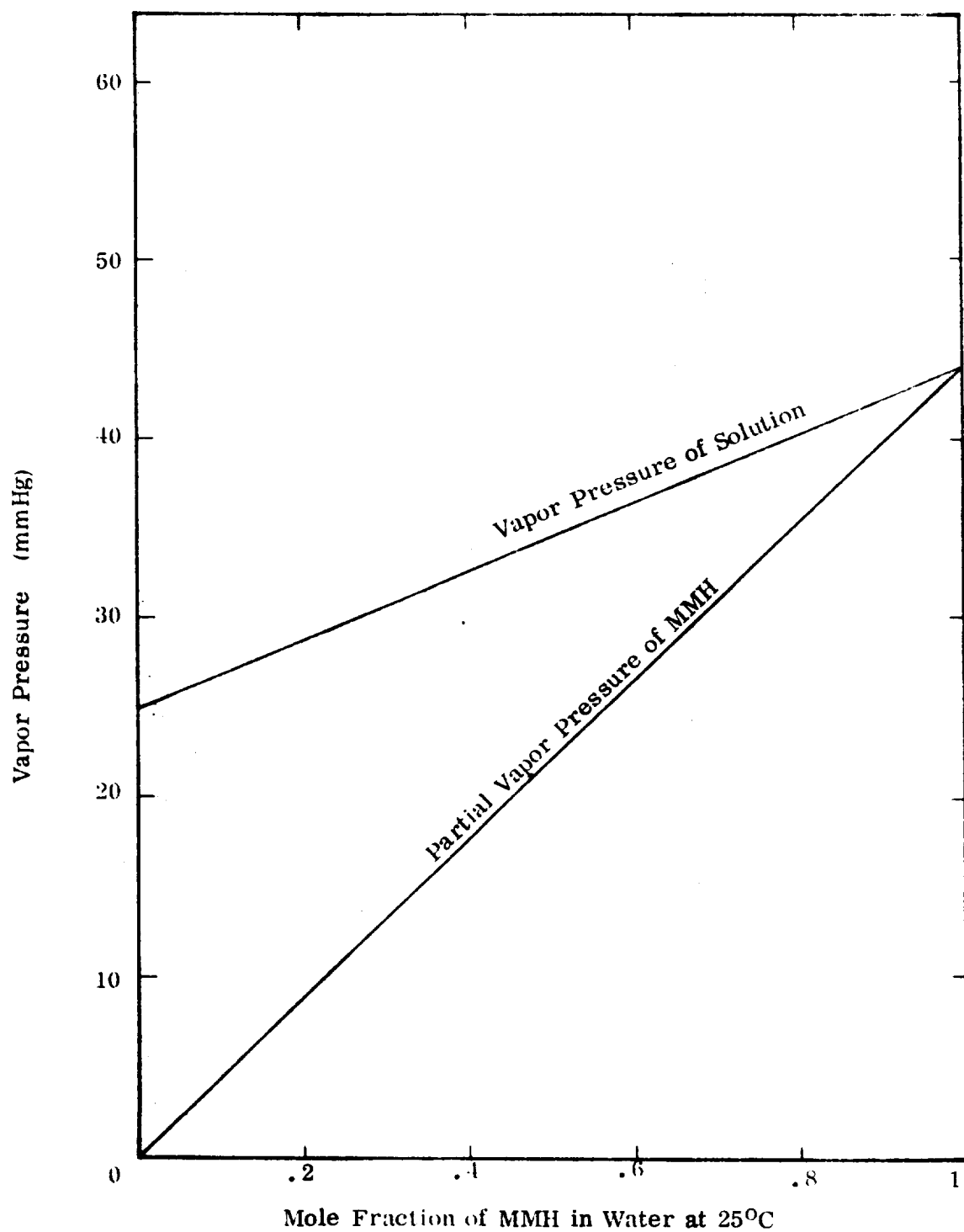


Figure 53. Vapor pressures of MMH/water mixtures.

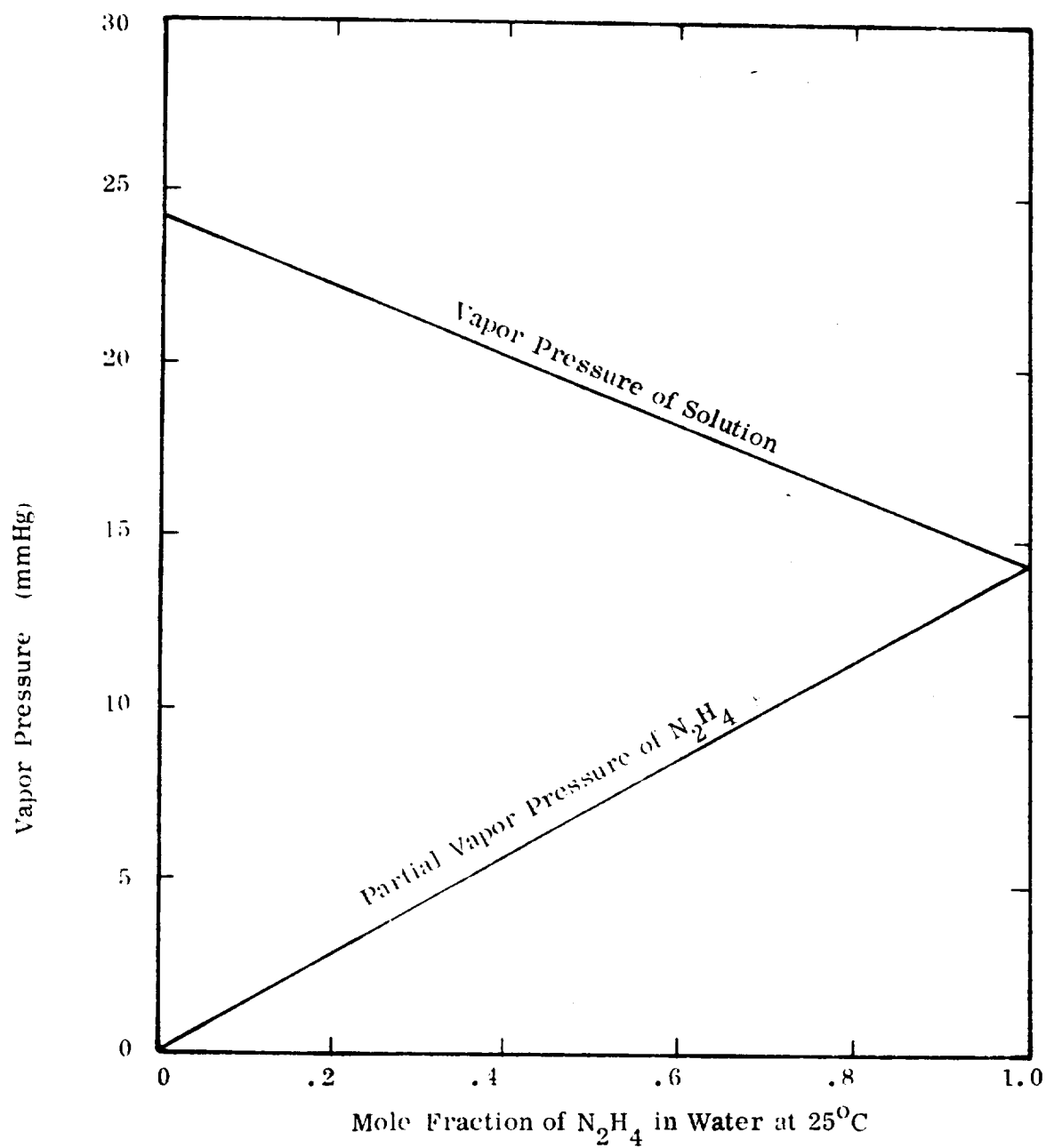


Figure 54. Vapor pressures of N_2H_4 /water mixtures.

2. Description of Countercurrent Scrubbers

In the countercurrent packed scrubber, the gas stream moves upward in a direction opposite the liquid stream which is moving downward through a packed bed (Figure 55). This method provides intimate contact between the liquid and gas streams within the packed beds and gives best results when the scrubber is operated at the maximum allowable pressure drop. At high pressure drops maximum turbulence is obtained, enhancing the quick absorption of the gaseous contaminants in the liquid stream.

A significant advantage of countercurrent flow is that the gas stream, rich in contaminants, comes into contact with the spent liquor at the bottom of the packed beds, while the fresh liquid coming in at the top of the scrubber is in contact with the least contaminated gas. This characteristic provides a fairly constant potential throughout the packed bed for driving the gaseous contaminants into the scrubbing liquid. There is also less chance that the dissolved gases will be stripped from the liquid.

Countercurrent flow scrubbers are more expensive to operate because of the high liquid consumption and high pressure drop. Since this design handles the tougher problem of removing gases, the higher cost of operation is balanced by the highly efficient absorption capability of removing gases with low solubility.¹

A detailed presentation of the calculations involved in establishing scrubber size in terms of incoming and outgoing mole fractions of contaminant in the liquid and gas streams, and total contaminant quantities, is found in the chapter by Seymour Calvert cited previously. Among the concerns are contact surface area, packing density, number of transfer units, height and cross-sectional area of the tower. Packing density is the ratio of total surface area to volume for the packing. For example, one inch Raschig rings have a packing density of 55 ft^{-1} .

¹Ceilcote, "Countercurrent Flow Scrubbers". Technical Bulletin 12-3, February, 1974.

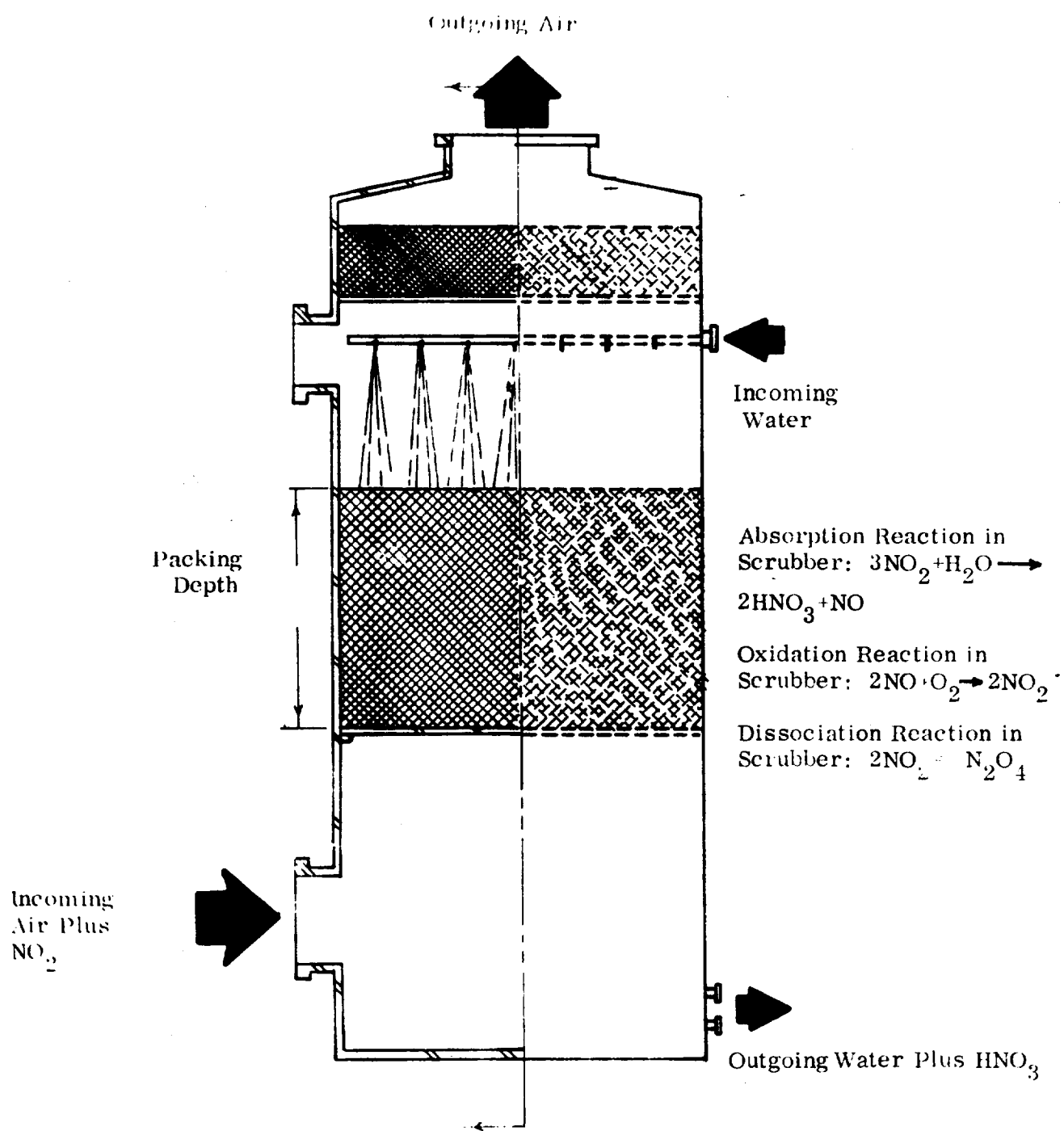


Figure 55. Counter current scrubber.

V. PRECIPITATION OF FLUORIDE FROM DILUTED IRFNA SOLUTION^{*}

OBJECTIVE: To determine how much fluoride can be removed from a diluted IRFNA solution by treating with a soluble calcium salt.

1. Introduction

IRFNA contains approximately 0.7% HF as a decomposition inhibitor. Fluoride is a highly toxic substance and its disposal into water streams (as occurs in the event of treating wastes) must be controlled to low limits set by the E. P. A. The solubility of calcium fluoride is given as 17 ppm. Theoretically, it should be possible to reduce the excess CaF_2 in solution to perhaps the 30-50 ppm level under suitable conditions. With this in mind the following procedure was tried.

2. Procedure

The IRFNA, as obtained from KSC, was diluted to a working solution approximating 2.2 to 2.6% nitrate and about 200 ppm fluoride levels. Na_2CO_3 was added to obtain a pH usually between 9.5 and 9.8. A solution of soluble calcium salt, as CaCl_2 or $\text{Ca}(\text{OH})_2$, was added in excess to provide the Ca^{++} ion in at least 2 to 5 times the stoichiometric quantity required for precipitating the contained fluoride ion. After standing from 1 to 24 hours to allow reaction or crystallization of CaF_2 , the treated solution was filtered through a millipore apparatus using a 0.45 micron pore size filter. Analyses were performed on original and filtered solutions for NO_3^- and F^- . The results of the 5 tests performed are discussed below.

3. Results

The results in Table XXXVII show that in the 5 runs made, the amount of fluoride removed was 46% in the best case and only 27% in the worst case. An average of the 5 percentages is 38%.

This is a poor showing, since the working solution contained about 200 ppm fluoride. With one third removed, the filtrate contained two thirds of the original amount, or about 100 to 150 ppm. If the solubility of CaF_2 is 17 ppm (in pure water) that figure is six to nine times greater than its solubility indicates.

4. Discussion

The poor results may be attributed to non-optimum conditions. Further, it is realized that NO_3^- interference may be contributing greatly. CaF_2 is slightly

^{*} Also see Appendix D

soluble in acid, particularly in HNO_3 which is a very good solubilizing agent. A much more dilute solution may have been more effective for fluoride removal. The concentration of HNO_3 in the runs was from 2.2% to 2.6%: perhaps sufficient to account for the low precipitation of CaF_2 .

It was decided, at this point, to discontinue additional laboratory work on this task and devote the effort to other tasks (reported herein) that were deemed to be more significant. Therefore, no gravity settling studies or tests under different conditions were performed.

5. Conclusions

On the basis of the above results, it was concluded that satisfactory removal of fluoride in a 2.2 to 2.6% NO_3 solution was not obtained by the method employed.

TABLE XXXVII
Data on Removal of Fluoride from Diluted IRFNA

Run #	Initial Concentration		Final Fluoride Concentration ppm	% Fluoride Removed	pH	Comments
	Nitrate ppm	Fluoride ppm				
1		205	150	27	9.8	
2	26,400	195	115	40	9.7	
3	26,400	150	80	46	9.7	Best result
4	22,000	170	105	38	9.5	
5	26,400	205	125	39	7.2	

Average ~38% fluoride removed

VI. FUME HOOD DESIGN CONSIDERATIONS

1. Introduction

Certain parts of the space shuttle will contain residual fuel after each flight. For maintenance these parts must be taken apart. Disassembly must be done such that personnel exposure to the hypergolic fuel (liquid and vapors) will be kept within tolerable limits.

A technique which will be used is to disassemble the part in a fume hood. A fan in the hood creates air flow, which carries the vapor away from the technician and vents it into the atmosphere or a scrubber. The hood also protects personnel from spills and splashes.

2. Calculating the Evaporation Rate

The hood considered for purposes of calculation of the evaporation rate has a table area of 12 square feet (3ft x 4 ft), an air flow rate of 6000 cubic feet per minute and an air velocity of 1000 feet per minute over the table. The evaporation rate was considered for the worst possible case - the fuel covering the entire table of the hood (12 ft²).

An empirical formula for water was used in lieu of specific information concerning the evaporation rates of the hypergolic propellants:

$$\dot{w} = .093 \left(1 + \frac{V}{230}\right) (e' - e) \quad (\text{Marks Mechanical Engineering Handbook})$$

where

$$\dot{w} = \text{rate of evaporation in lbs/hr ft}^2$$

$$V = \text{Velocity in ft/min}$$

$$e' = \text{Vapor pressure of liquid, as a function of temperature, in inches of mercury}$$

$$e = \text{Vapor pressure of substance in the incoming air in inches of mercury}$$

Letting $V = 1000$ ft/min (5.08 m/sec, or 11.36 miles per hour) and $e = 0$ gives the result

$$\dot{w} \approx 0.5 e'$$

Using this equation, the following maximum evaporation rates were calculated for various hypergolic propellants at 10°C and 20°C. The 20°C temperature is for evaporation at ambient temperature, the lower temperature is an estimate to account for evaporative cooling of the spill.

	<u>10°C</u>	<u>20°C</u>
N ₂ H ₄	1.8 lbs/hr	2.88 lbs/hr
MMH	1.8 lbs/hr	7.2 lbs/hr
N ₂ O ₄	140 lbs/hr	180 lbs/hr
H ₂ O ₂	.45 lb/hr	.54 lb/hr

These quantities would be mixed with 28,000 pounds per hour of air resulting in the following concentrations (by weight) in parts per million.

	<u>10°C</u>	<u>20°C</u>
N ₂ H ₄	64.5	100
MMH	64.5	358
N ₂ O ₂	5000	6450
H ₂ O ₂	16.1	19.3

3. Effluent Scrubbing

The question of the treatment of effluent air from hypergolic fuel fume hoods has been considered and the results are summarized in Figures 56 and 57. Results indicate that it would be satisfactory under most conditions to simply vent effluent from a hood through a 10:1 air mixing section into the atmosphere. A scrubber may well be used, but should not be considered a necessity.

The calculation upon which the conclusion is based is relatively conservative in that a flooded hood table is assumed, a rather high flow speed (1000 ft/min) over the hood table is assumed, and UDMH (with a relatively low boiling point and high vapor pressure) is considered.

SMALL PARTS HANDLING HOODS

APPROPRIATE FOR EITHER HYDRAZINES OR FOR N_2O_4
& NO_2 IN MODERATE QUANTITIES.

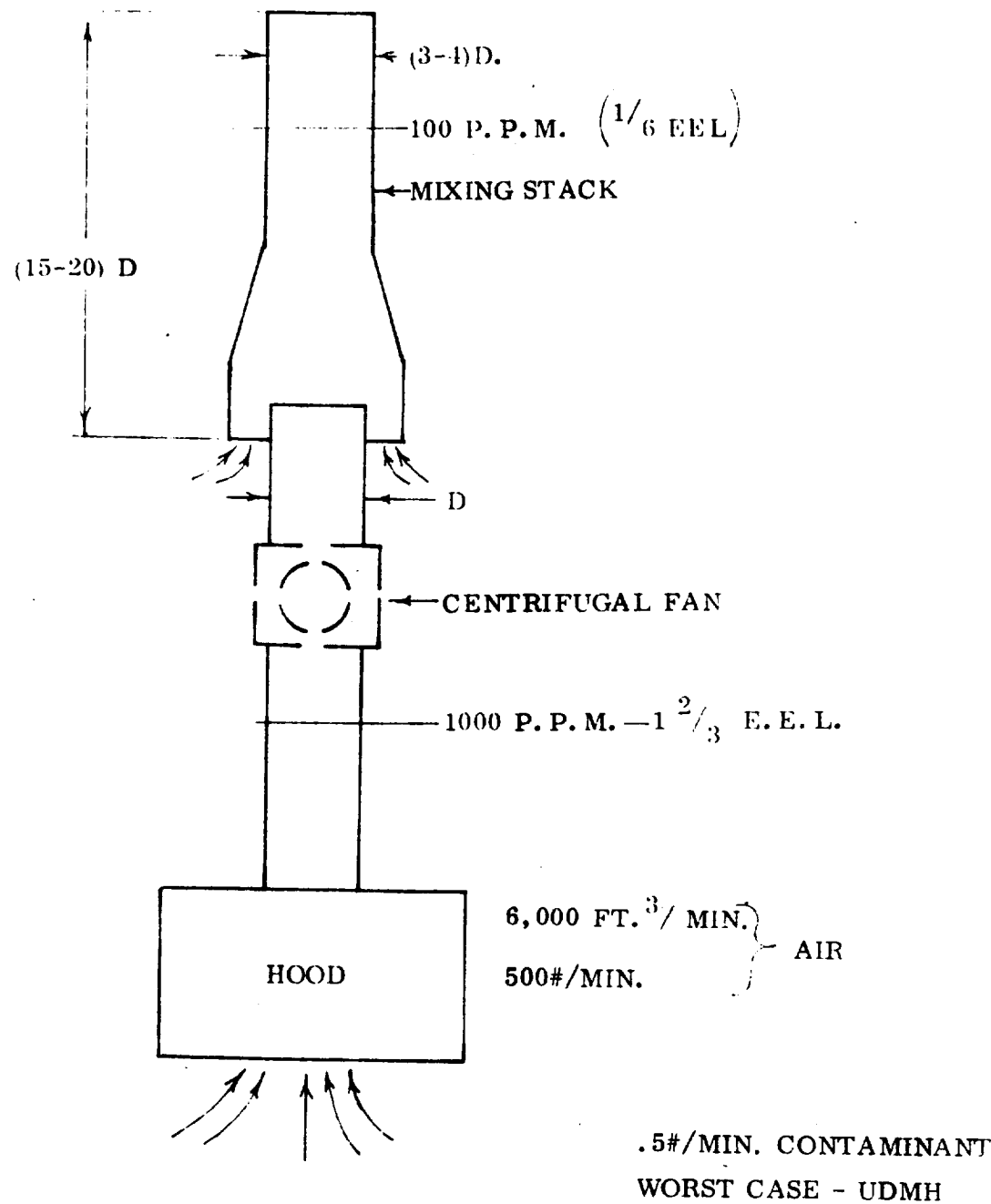


Figure 56. Fume hood with air mixing section.

WORST CASE EXAMPLE

UDMH SATURATED MASS FRACTION W/ N_2 AT \sim S. T. P.

.358 (OTHER HYDRAZINES LOWER) EVAPORATION
OF UDMH FROM FLOODED HOOD TABLE

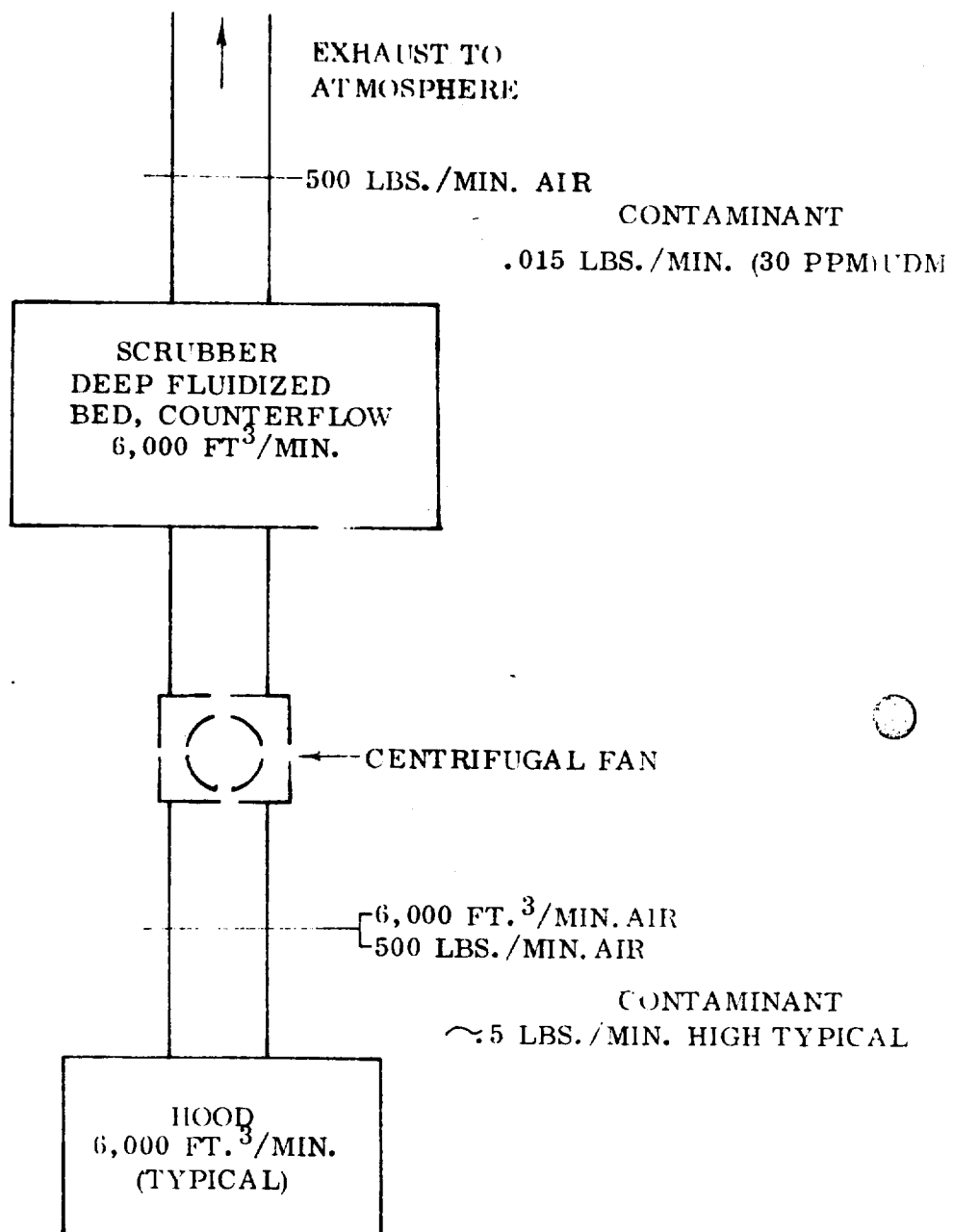


Figure 57. Fume hood with scrubber.

VII. WASTE HANDLING AND FACILITY LOCATION CONSIDERATIONS

A. SOURCES OF, AND DISPOSAL SITES FOR, SPACE SHUTTLE HYPERGOLIC PROPELLANT WASTES

1. Introduction

In general, holding ponds and reaction ponds are recommended for contaminant disposal in preference to burners - flare burners or sudden expansion burners. The holding ponds are generally cheaper than burners, do not require the auxiliary fuel which burners need, and they are quieter, easier to operate, operate at lower temperature, and require less frequent monitoring and attendance.

On the other hand, ponds probably can accept only liquids, so that scrubbers are required for vapors - see Section VI of the portion of this report on "Alternative Disposal Concepts," however, for an investigation of direct vapor phase addition of N_2O_4 to holding ponds. Ponds require more space, and often result in longer-term rather than immediate disposal. Again, however, some of our work reported in earlier sections has been concerned with ways of obtaining faster decomposition in holding ponds.

While holding ponds are less portable than burners, this disadvantage is probably not serious except in the case of the contingency landing site. The tools to carve a holding pond are usually close at hand, and lining material can be moved in easily and assembled. Combustors would still have their place where disposal action needs to be initiated as quickly as possible and completed as soon as possible.

2. Launch Site

During the fueling operation approximately 480 gallons of nitrogen tetroxide and substantial MMH might be vented into the air and an undetermined quantity might be spilled. The liquid can be removed from the contaminated area by flushing the surface with water or by evaporation. The vapors can be removed from the vent gas by scrubbing. Scrubbing removes noxious gases from the air stream by a gas absorption process. This process involves the transfer of the vapor from

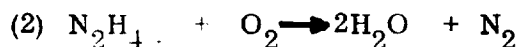
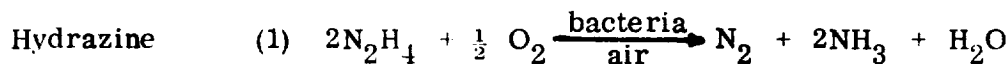
the gas phase into a liquid in which it is soluble. This process is dependent on the solubility of the gas in the liquid and the intimate contact the gas makes with the liquid.

Another method for recovering the N_2O_4 vapors is recondensation. Recondensation involves cooling a mixture of gases below the dew point of the constituent to be removed and collecting the condensed liquid in a suitable container. The part (or percentage) of the contaminant which is removed by recondensation depends on the temperature that the mixture can be cooled to, as well as the constituents of the mixture itself, and can be quite small. The use of recondensation to recover vaporized fuel awaits further development.

Once the wastes have been collected they must be transferred to a disposal site about 1000 feet away. Since the scrubbers, if used at the launch site, would be located 50 feet above the surrounding ground level, gravity may be used to transport the liquid from the scrubber. The distances involved do permit a drop/run ratio of 1/20 in the drainage system and two 6 inch pipes may prove to be appropriate for the flow rates from scrubbers.

The proposed disposal site is located approximately 1000 feet south of the center of the launch pad (Figure 58). The 1000 feet gives an ample downwind clearance at all points on the pad and is outside the 700 foot downwind safety perimeter of the two existing fuel bunkers. Its position near the proposed storage tanks leaves room immediately north of the pad for further development without vapors from the ponds creating a potential safety hazard.

There are several types of ponds proposed. In an oxidation pond, the fuels are allowed to react with dissolved oxygen with the help of bacteria according to the equations:



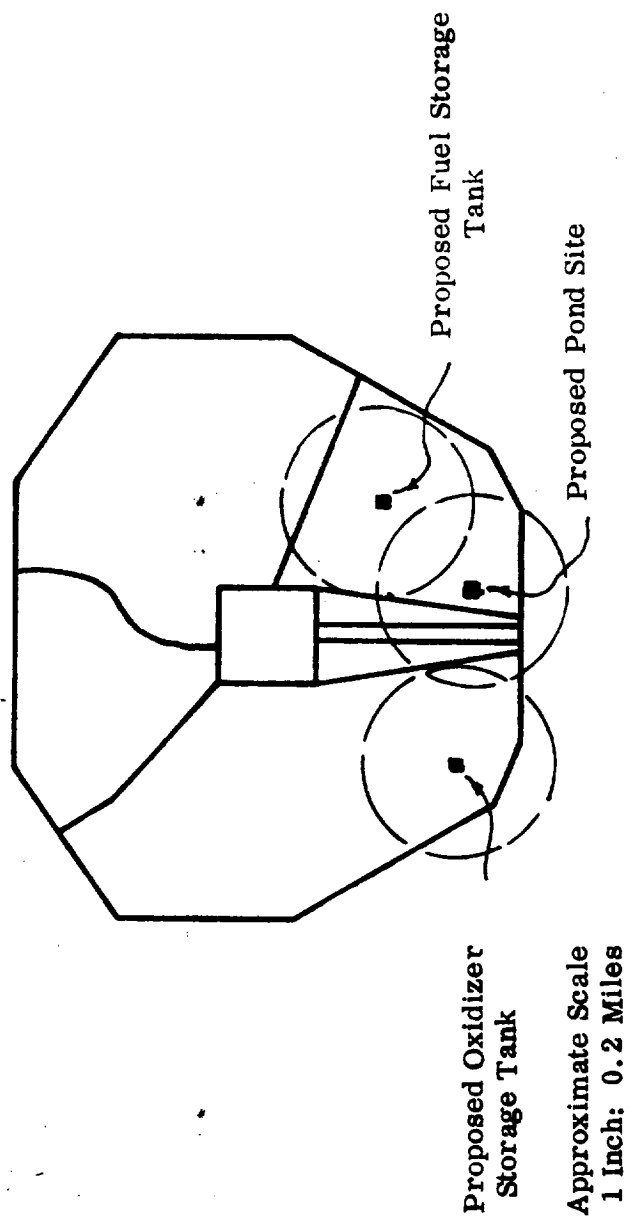
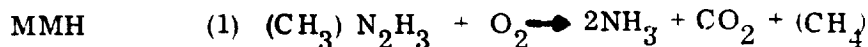
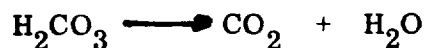
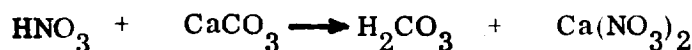
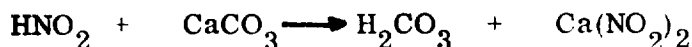
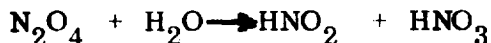


Figure 58. Launch complex 39-A and 39-B.

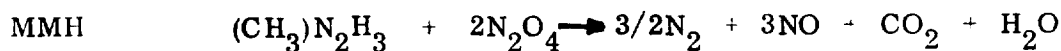
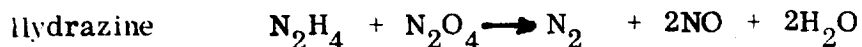


A neutralizing pond is where the oxidizer, N_2O_4 , reacts with calcium carbonate in an aqueous solution according to the following reactions:



or, indeed, where any of the propellants reacts with any sort of neutralizing reagent, as described in the portion of this report on "Evaluation of Current Disposal Concepts."

A reaction pond is where the fuel and oxidizer are allowed to mix and react; for example:



Since more NO_2 or N_2O_4 is expected to be emitted from the fueling process than MMH*, it is expected that collected MMH emissions will be insufficient to neutralize collected NO_2 emissions and another neutralizer such as CaCO_3 will have to be used in the holding pond at the launch area.

* As a result of its higher vapor pressure.

3. Orbiter Processing Facility

At the end of each flight the shuttle will be disassembled at the orbiter processing facility. At the O. P. F. large quantities of concentrated and dilute propellants will have to be dealt with. Two scrubbers at the O. P. F. with an air flow rate of $40,000 \text{ ft}^3/\text{min}$ and a liquid flow rate of 600 GPM will produce effluent at the rate of $2.8 \text{ ft}^3/\text{sec}$. If this effluent is to be piped to a pond, two pipes 8 inches in diameter, each fitted with a 1.5 Hp pump, may be a suitable combination to transport the liquid. The residual fuel may be collected in a tank truck or drums.

The location of the proposed pond is about 2000 feet west of the O. P. F. (Figure 59). This position gives a safety perimeter of more than 700 feet from the O. P. F., V. A. B. and other nearby facilities as well as the highway.

4. Hypergolic Maintenance Facility

At the hypergolic maintenance facility, small parts from the shuttle containing small quantities of hypergolic fuels will be cleaned and repaired. These parts will be disassembled under a hood and the air stream from the hood may be scrubbed to remove the vapors. If done, this will create small quantities of diluted fuels.

At the hypergolic maintenance facility four hoods with an air flow rate of $6000 \text{ ft}^3/\text{min}$ and a liquid flow rate of $0.2 \text{ ft}^3/\text{sec}$ is assumed for purposes of estimation. The total rate of liquid discharge for the four hoods is $0.8 \text{ ft}^3/\text{sec}$.

Once these wastes are collected, they must be transported to a holding pond about 200 feet or more away from the scrubbers (Figures 60 and 61). This may be done by piping the effluent to the pond. Since only 5 feet of head is created due to the difference in liquid height a pump may be required to supply a sufficient head to overcome the friction head in a 5 inch pipe. A larger pipe with appropriate traps may be used in lieu of the 5 inch pipe and pumps. Since small quantities of diluted hypergolic fuels will have to be disposed the

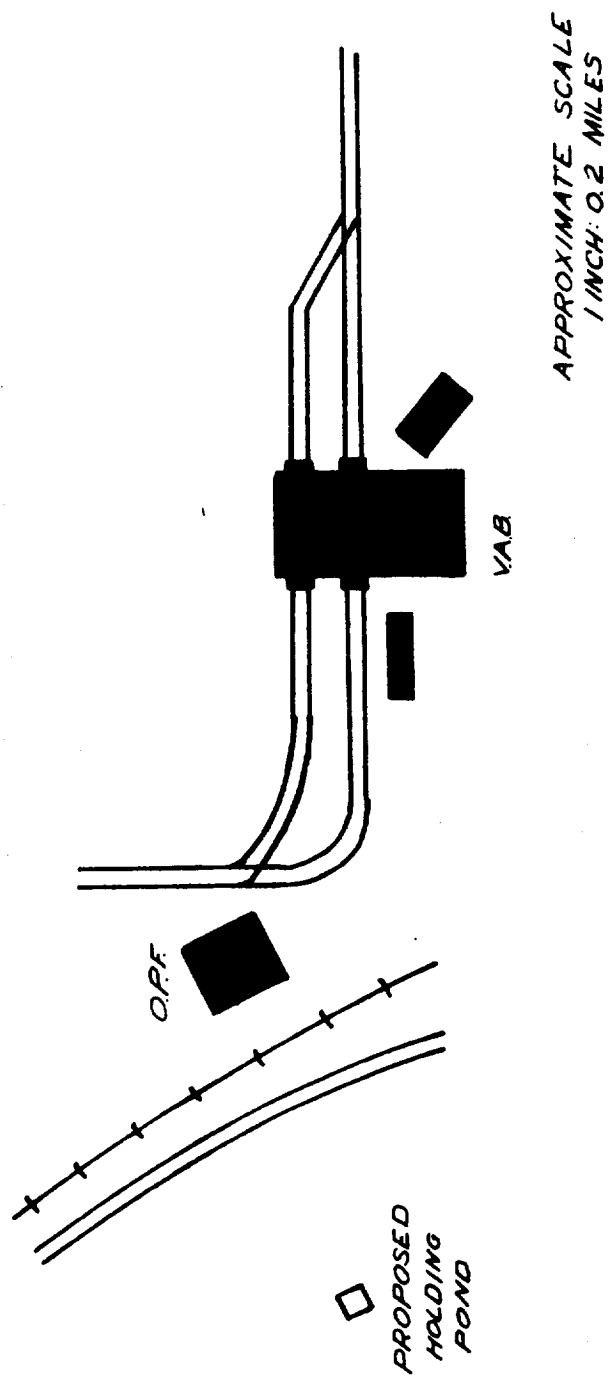


Figure 59. Orbiter processing facility

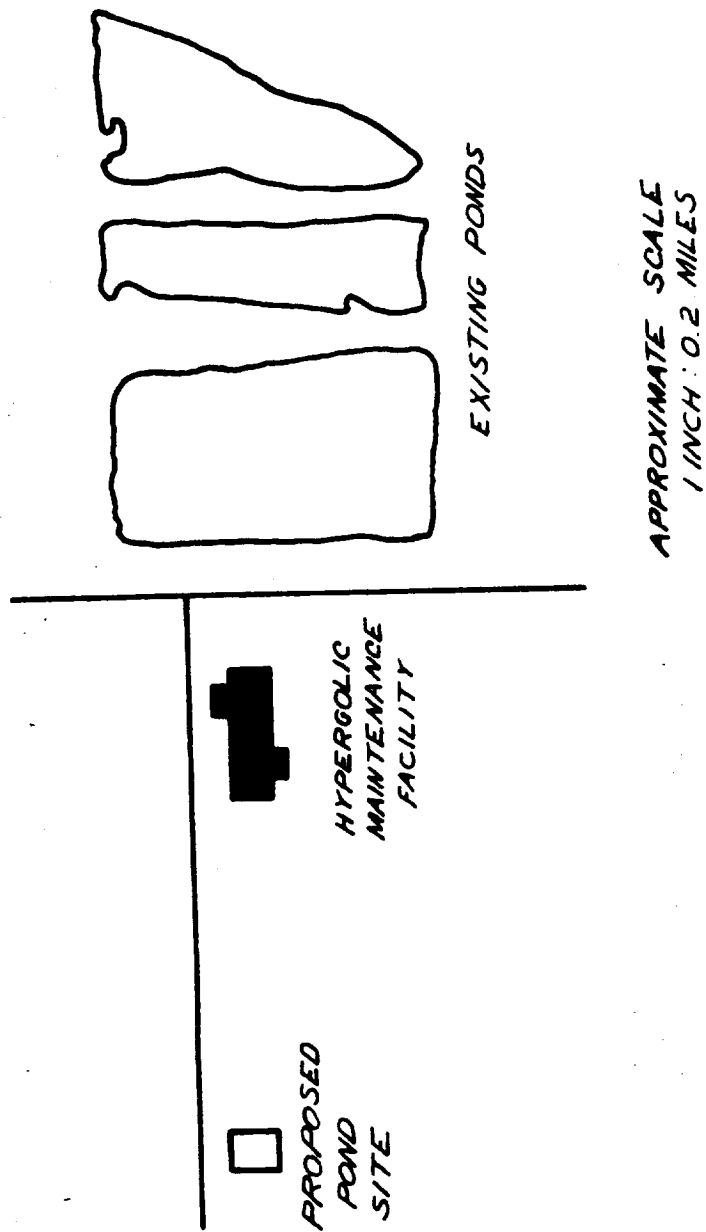


Figure 60. Hypergolic maintenance facility

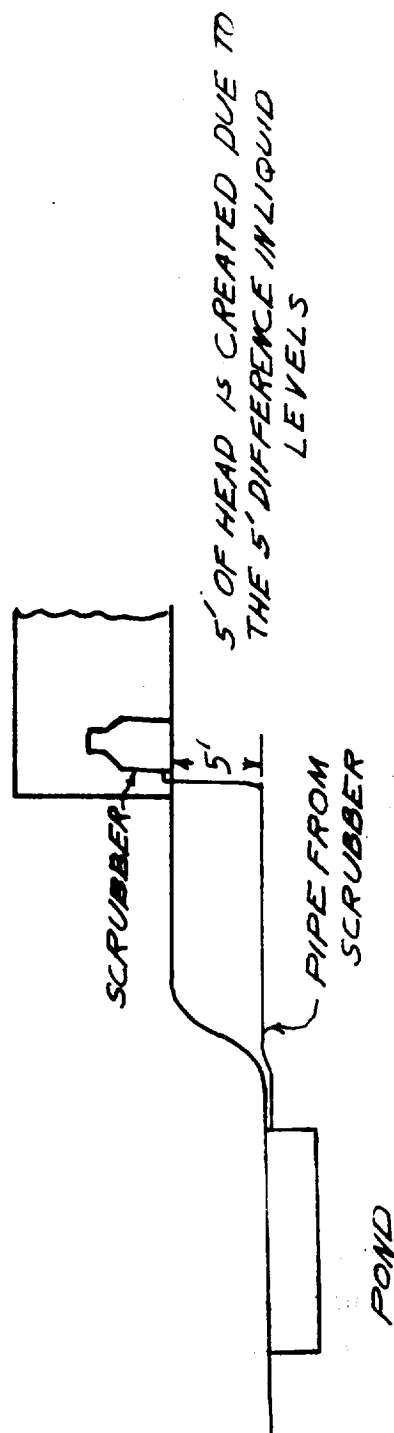
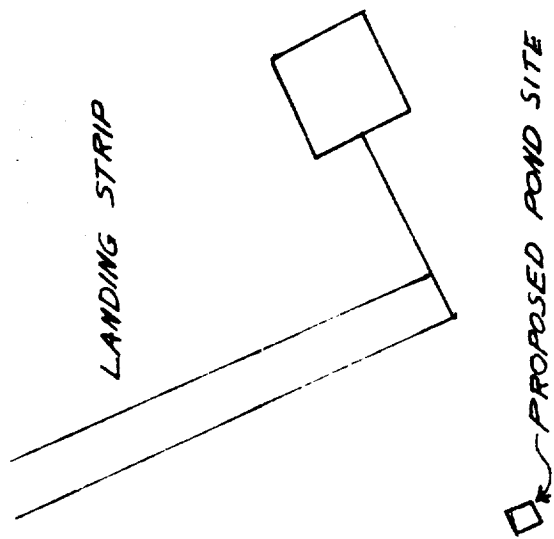


Figure 61. Hypergolic maintenance facility

safety perimeter can be less than 700 feet. The diluted fuel can be piped to a pond 200 feet east of the hypergolic maintenance facility provided the pond is lined with a suitable material. A holding pond may also be constructed 200 feet west of the hypergolic maintenance facility.

5. End of Runway

If a shuttle should be leaking fuel upon landing it may be desirable to dump the fuel as near the landing site as possible, rather than tow the vehicle to the O. P. F. The fuel may be transferred into a tank or pumped to a nearby pond (Figure 62.)



APPROXIMATE SCALE
1 INCH = .5 MILE

Figure 62. Landing site

B. ROUGH COST ESTIMATES FOR TRANSPORTATION OF HYPERGOLIC WASTES FROM COLLECTION TO DISPOSAL SITES

1. Introduction

At the launch site vapors from the hypergolic propellants are vented at the rate of 3 gal/min during the loading operation. It may be necessary to remove these vapors from the air by scrubbing. Scrubbing produces a fuel plus water solution which must be treated at a holding pond or elsewhere. Any fuel spills which occur must be washed with water or other solvents which produces an effluent that must be transported to a holding pond for treatment.

At the landing site residual fuels must be disposed of before the shuttle is taken to the O. P. F., which means transporting the propellants from the shuttle to a treatment facility.

Several means of transporting the propellants are considered.

2. Transporting the Effluent in Drums

One method considered is to transport the waste in 55 gallon drums or a tank truck. At the landing site small quantities of concentrated fuels will have to be dealt with. If the hypergolic fuel vented in the transfer from the shuttle to the drum or tank truck can be kept within tolerable limits, the use of stainless steel drums may be the most economical method of transporting the propellants.

3. Some Initial Cost Estimates for Transporting Fuel From the Landing Site to the Holding Pond.

a. Using Stainless Steel Drums and a Truck

30 - 55 gal. S. S. drums	@	\$208 each	-	\$6000
1 truck - flat bed	@	\$5000 each	-	<u>\$5000</u>
				\$11000

b. Using 1000 gal. Stainless Steel Tank Truck

1	1000 gal tank	@ \$2230	-	\$2230
1	truck	@ \$3500	-	<u>\$3500</u>
				\$5730

c. Using 3000 gal. Stainless Steel Tank Truck

1 -	3000 gal tank	@ \$6800	-	\$6800
1	truck	@ \$5000	-	<u>\$5000</u>
				\$11800

4. Pumping the Effluent

To transport the water-fuel solution from the launch pad to the holding pond the pump must overcome the pressure head plus the friction head. For calculation purposes it was assumed that the flow rate of liquid from the scrubber was 1.33 ft³/sec (600 gpm), the head 10 feet and the pipe 1000 feet long and relatively straight. Various diameters of pipe were chosen and the loss of head per 1000 feet of pipe was found on a pipe-flow diagram. By knowing the loss in head the horse power needed to pipe the liquid was calculated by the following equation:

$$H_p = 1.48 + .148 X$$

where X is the loss of head in feet. The pipe diameters with the corresponding friction heads and required pumping horsepower are as follows:

Diameter of Pipe	Friction Head	Horsepower Required
3 inches	800 feet	118
6 inches	35 feet	5.2
9 inches	5 feet	3.25
12 inches	1 foot	1.62

These estimates are made for the very high flow rate that was assumed. The flow rate was based on a requirement for 99% removal of NO₂ from an air stream containing small amounts of NO₂ initially; for many applications, much smaller flow rates are anticipated.

Flow rates in fueling site scrubbers are based on the steady-state assumption; assumption of the use of single-pass countercurrent scrubbers; a contaminant loss rate of 3 GPM; contaminant weight fraction concentration in the outlet gas just below the 1 hour E. E. L. - 10 ppm for MMH and 7 ppm for NO_2 ; and a 99% contaminant removal in the scrubber.

It follows that the weight fraction of NO_2 in the scrubber inlet gas is 7×10^{-4} and of MMH is 10^{-3} . At equilibrium (implying a scrubber of infinite length), from the equilibrium curves of Section III. C. 1, the weight fraction of HNO_3 in the water outlet of the scrubber is 2×10^{-2} and of the MMH at the scrubber water outlet is 10^{-1} . A 3GPM flow of N_2O_4 implies 34 lbs/min while a 3 GPM flow of MMH implies a 22 lbs/min flow. Thus the minimum water flow rates under these conditions in infinitely long scrubbers are $(34/2 \times 10^{-2})$ lbs/min or 215 GPM in the NO_2 scrubber, and $(22/10^{-1})$ lbs/min or 28 GPM in the MMH scrubber. These flow rates would increase substantially to provide the transport potential necessary in a finite length scrubber.

Although stainless steel might be required for pipes carrying these propellants at the launch site, it may be feasible in some applications to use a cheaper material that is resistant to diluted fuels, such as polyethylene or P. V. C.

5. Some Initial Cost Estimates for Transporting Fuel from the Launch Pad to the Holding Pond

a. Stainless Steel Pipe -

9 inches in diameter 3/16 inch thick, at \$38 per foot, will cost \$38,000 per 1000 feet.

b. Cast Iron Pipe -

9 inches in diameter, 1/2 inch thick, at \$25 per foot, will cost \$25,000 per 1000 feet.

c. Excavation

2 - 3 feet deep, at \$1.50 per foot, will cost \$1500 per 1000 feet.

8 - 12 feet deep at \$10 per foot, will cost \$10,000 per 100 feet.

d. Stainless Steel Drums

55 gal., 23 inches in dia. by 35 inches high at \$208 per drum, will cost \$47,500 for 227 drums.

C. DUMPING OF HYPERGOLIC PROPELLANTS FROM DRUM TYPE CONTAINERS

1. Description of Dumper

A commercially available dumping device (Figure 63) such as manufactured by the HERCULES INDUSTRIES CO., their Catalog No. HI-110, or equivalent, is recommended. The dumper can handle various size drums up to 24 inches in diameter and has a lifting capacity of 750 lbs. The drum is securely clamped into a concave cradle and swung through an arc of 135 degrees, stopping at an angle of 45 degrees above horizontal. The dumper is powered by an explosion proof electric motor and a hydraulic cylinder. It can be modified for remote control by installing an additional motor control switch, and extending the needle valve control using a flexible shaft to the remote site. List price of the dumper is \$1125.00

2. Description of Drums

Drums should be the end opening type, one large tapped hole near the edge for filling and emptying and one small tapped hole diametrically opposite for air venting. Both holes should have manually operated valves in closed position.

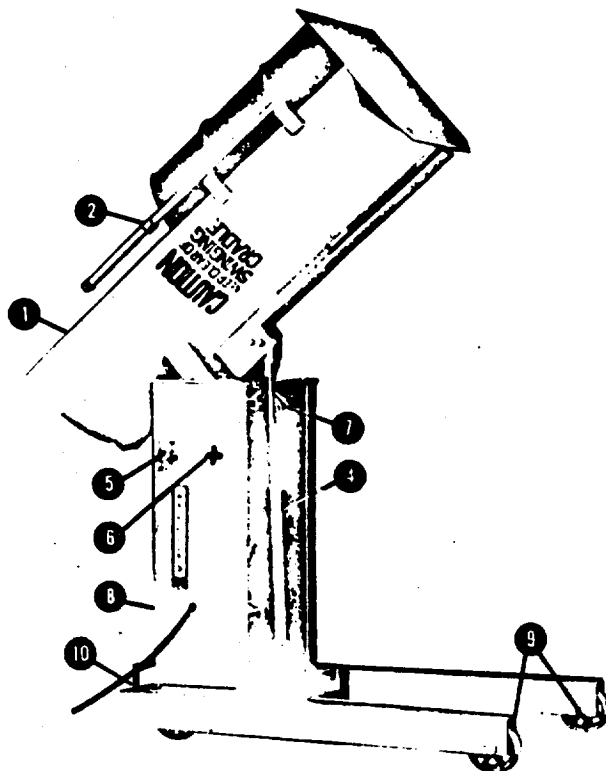
3. Loading Drums into Dumper

Loading a full 55 gallon drum will require a hoisting device and a Grizzly No. 235 Vertical Drum Lifter (Figure 64). The drum is placed in the dumper with the large valve forward and clamped securely with the adjustable hold-down clamps.

4. Dumping Operation

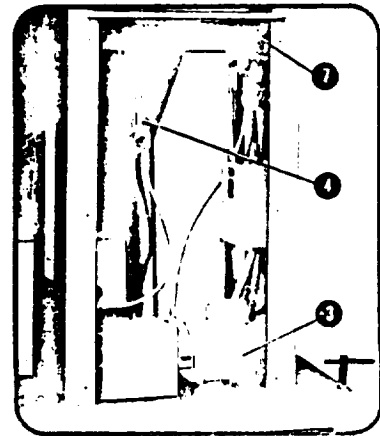
To prevent wind-borne spray and vapor escape during the dumping operation, a stainless steel flexible hose is attached to the large valve on the drum and the other end of the hose placed in the disposal facility (Figure 65). Both valves are then opened. All personnel should be cleared from the area and the dumping

HERCULES LOW-LEVEL DUMPER



- ① 3/16" STEEL CONCAVE DUMPING CHUTE
- ② ADJUSTABLE HOLD-DOWN CLAMPS
- ③ ELECTRIC MOTOR AND HYDRAULIC PUMP UNIT
- ④ DUMPING LIFT CYLINDER AND CHROME-PLATED RAMS
- ⑤ PUSH BUTTON CONTROLS

- PORTABLE OR STATIONARY MODELS
- HANDLES EITHER STEEL OR FIBRE CONTAINERS — UP TO 24" IN DIAMETER
- 750, 1000 AND 1500 POUND STANDARD CAPACITIES, INCREASED CAPACITIES AVAILABLE
- SERVICES HEIGHTS FROM 36" TO 60"



- ⑥ MANUAL NEEDLE VALVE LOWERING
- ⑦ FLANGE-MOUNTED PILLOW BLOCK BEARINGS
- ⑧ 3/16" STEEL SIDE PLATES
- ⑨ 6" DIAMETER LOAD WHEELS AND CASTERS ON PORTABLE MODELS
- ⑩ SCREW-DOWN LOCKS ON PORTABLE MODELS

Figure 63. The Hercules dumper.



Grizzly®

NO. 235 VERTICAL DRUM LIFTER

U. S. PATENT No. 2,764,447

2000 LBS. CAPACITY

FOR OPEN

or

CLOSED DRUMS

USED WITH

Fork Trucks

Chain Falls

Cranes and Hoists

- **QUICK** — Lifter attached and removed in seconds.
- **SAFE** — Fast turning crank handle to lock Upper Jaw to drum top. Holds drum rigidly even when swaying or when bumped.
- **VERSATILE** — Lifter moves 55 and 30 gallon, and even smaller steel drums with practically no manual labor — the lifter does the work.
- **LIGHT** — Weighs only 32 pounds. One man can handle with ease.
- **ADJUSTABLE** — Slide Lower Jaw on vertical bar to position below nearest chime of drum. Jaw rests on off-center cam.
- **LIFTS** — Old and new drums, open or closed, battered or lopsided.
- **STACKS** — and tiers drums vertically in close quarters.
- **RUGGED** — All welded construction.

• **FINISH** — Safety Orange.

SHIPPING WEIGHT 32 LBS.

PRICE \$60.00

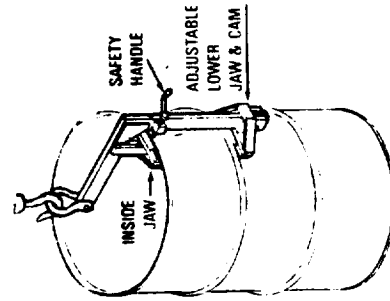
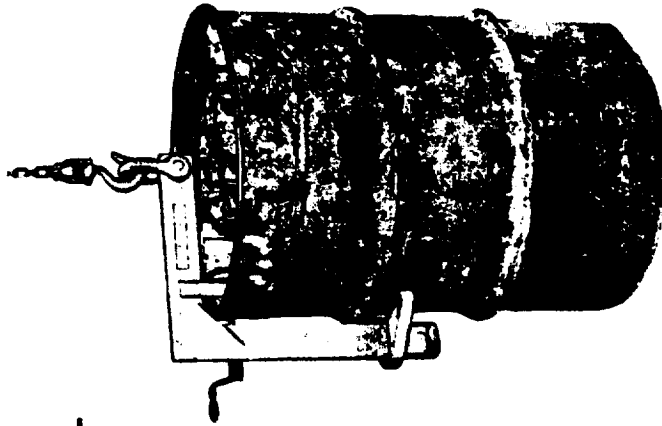


Figure 64. Grizzly vertical drum lifter.

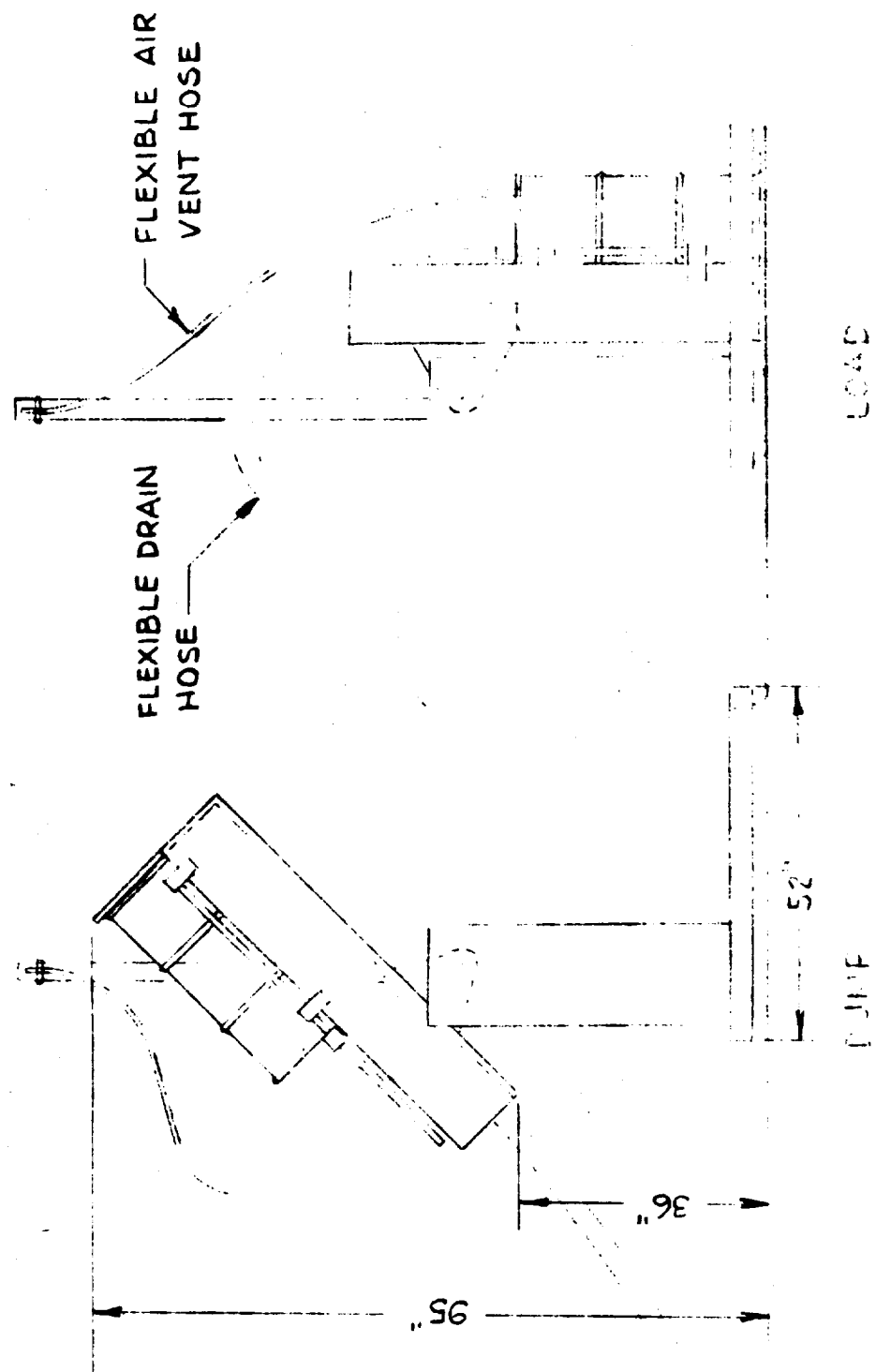


Figure 65. The dumper in dump and load positions.

controlled from a site at least 10 ft. remote. Actual flow of the liquid into the hose does not start until the drum is swung approximately 30 degrees from vertical. At this point accurate and sensitive control of the swing velocity should be maintained to ensure the level of the liquid does not rise so fast as to flow out of the air intake vent.

A means of controlling the slack in the hose induced by the swinging action of the drum can best be determined by trial. Should it prove impractical to maintain accurate and sensitive control of the swing velocity, an alternate method to prevent leakage from the air vent is possible by attaching a mast to a stationary portion of the dumper and extending a flexible hose from the air vent on the dumper to the top of the mast. The highest point of the hose should be higher than the highest point of the drum at full dump position.

VIII. ASPECTS OF DISPOSAL AT CONTINGENCY LANDING SITES

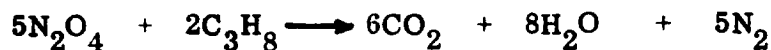
1. Introduction

If the shuttle should be forced to make an emergency landing at a contingent landing site that does not have the proper facilities to dispose of the fuels, the problem arises as to how these propellants can be disposed of safely, economically, and in an ecologically safe way. Up to 30,500 Kg (8000 gal) of hydrazine and 42,000 Kg (8000 gal) of nitrogen tetroxide could be on board the shuttle when it lands. Many different means of resolving the problem are available; here a few will be considered.

2. Disposal Methods

a. Using a Flare Burner to Dispose of Nitrogen Tetroxide

The flare burner is used to dispose of nitrogen tetroxide by igniting a mixture of N_2O_4 vapors and hydrocarbon fuels. The stoichiometric equation for this reaction (propane assumed) is:



Satisfactory operation can be obtained at over-stoichiometric conditions (fuel-rich).

A weight ratio of propane to N_2O_4 which is a little less than .45 results in less than 200 parts per million NO production ⁽¹⁾. To dispose of 42,000 Kg (92,400 lbs) of N_2O_4 would require 18,900 Kg (41,600 lbs) of propane. Such flare burners could be fired by other hydrocarbon fuels. The flare burner has a fuel flow rate of .076 Kg/sec (10 lbs/min) and would require about 6 days to get rid of the nitrogen tetroxide.

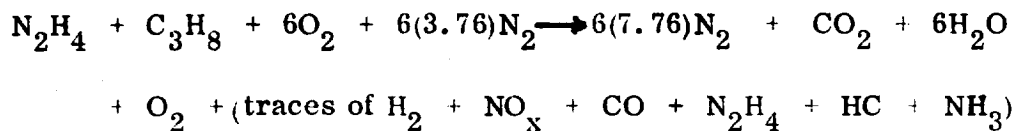
b. Disposing of N_2H_4 by Bubbling Air Through a Water-Fuel Mixture or by Destroying it in a Sudden Expansion (SUE) Burner.

At the contingent landing site a SUE burner or an aerated holding pond may be used to destroy the hydrazine. In the holding pond air oxidation and

¹See page 113.

bacterial action slowly convert hydrazine into nitrogen, ammonia and water. Aeration by bubbling air through the fuel-water solution will accelerate the decomposition by making oxygen readily available to the hydrazine. The use of copper sulfate as a catalyst will further speed the decomposition; see Section III. A. above. The holding pond would probably have to be built on the spot, when needed, to a standard design. It is possible that a portable unit-perhaps in sections - could be designed.

An alternate method of disposing hydrazine would be to use a SUE burner. It can incinerate hydrazine at the rate of .146 liter/sec (140 gal/hr), taking about 57 hours to burn 30,500 Kg (8000 gal) of hydrazine. The SUE incinerator renders the hydrazine into environmentally safe products according to the reaction.



c. Mixing Fuel and Oxidizer Stoichiometrically in a Holding Pond

An advantageous alternative to using the flare burner to dispose of N_2O_4 and the holding pond or SUE burner to dispose of the hydrazine would be to mix both the N_2O_4 and the hydrazine in a holding pond of suitable size. In the holding pond the fuel and oxidizer can be mixed in the proper ratios to neutralize one another. The chemical reaction is exothermic and the temperature of the pond will increase.

To accommodate the amount of fuel on the shuttle, while keeping the pond within 30°C of ambient temperature would require 2820 cubic meters (8.9×10^5 gal) of water (see Section II. A. above). This process is relatively safe, the products of the reaction evolving as harmless gases. A possible problem is that N_2O_4 boils at 21°C (71°F) at sea level, and still lower temperature at higher elevations, making it difficult to dispose of if the temperature of the pond is greater than this boiling point. Two possible solutions would be pre-dilution in cold water then releasing it into the holding pond, or slowly releasing the N_2O_4 from the bottom of the fuel rich pond and allowing it to

react with the fuel as it bubbles to the surface. If the pond is deep enough, hydrostatic pressure will help to prevent vapor formation. Roughly speaking, the boiling point of N_2O_4 increases one degree Fahrenheit for each foot of pond depth, at $68^\circ F$.

d. Evaluation

The disadvantage of the flare burner is that it requires large quantities of hydrocarbon fuels to destroy the N_2O_4 . Since about 19,000 Kg (42,000 lbs) of propane would be needed to dispose of the N_2O_4 on the shuttle and since the price of fuels is increasing, the cost of disposing N_2O_4 by this method may be exorbitant. The combustion of the flare burner must be carefully monitored because operating it in an oxidizer rich mode will result in the emission of hot NO and NO_2 gases. If the flare burner is used, a method to dispose of the hydrazine must be used in conjunction with the flare burner.

The hydrazine could be decomposed (air oxidation) in a holding pond, or neutralized with the N_2O_4 or it could be destroyed in a SUE burner. One disadvantage of using a holding pond is the lack of portability; it might have to be constructed wherever the shuttle would land. The holding pond could take several days to construct. It would be used only once, which would make this method economically questionable. On the other hand, it is possible that an air transportable holding pond, perhaps using stainless steel or plastic modules, could be designed.

The SUE burner would have the portability but it also requires a supplementary fuel.

APPENDIX A

VAPOR PRESSURE AND DISSOCIATION CURVES

These curves are plots of the empirical equations presented in Section II. A of the portion of the report on "Alternative Disposal Concepts."

Figure A-1: Vapor Pressures of N_2H_4 , MMH, and UDMH

Figure A-2: Vapor Pressure of N_2O_4 - NO_2

Figure A-3: Dissociation of N_2O_4

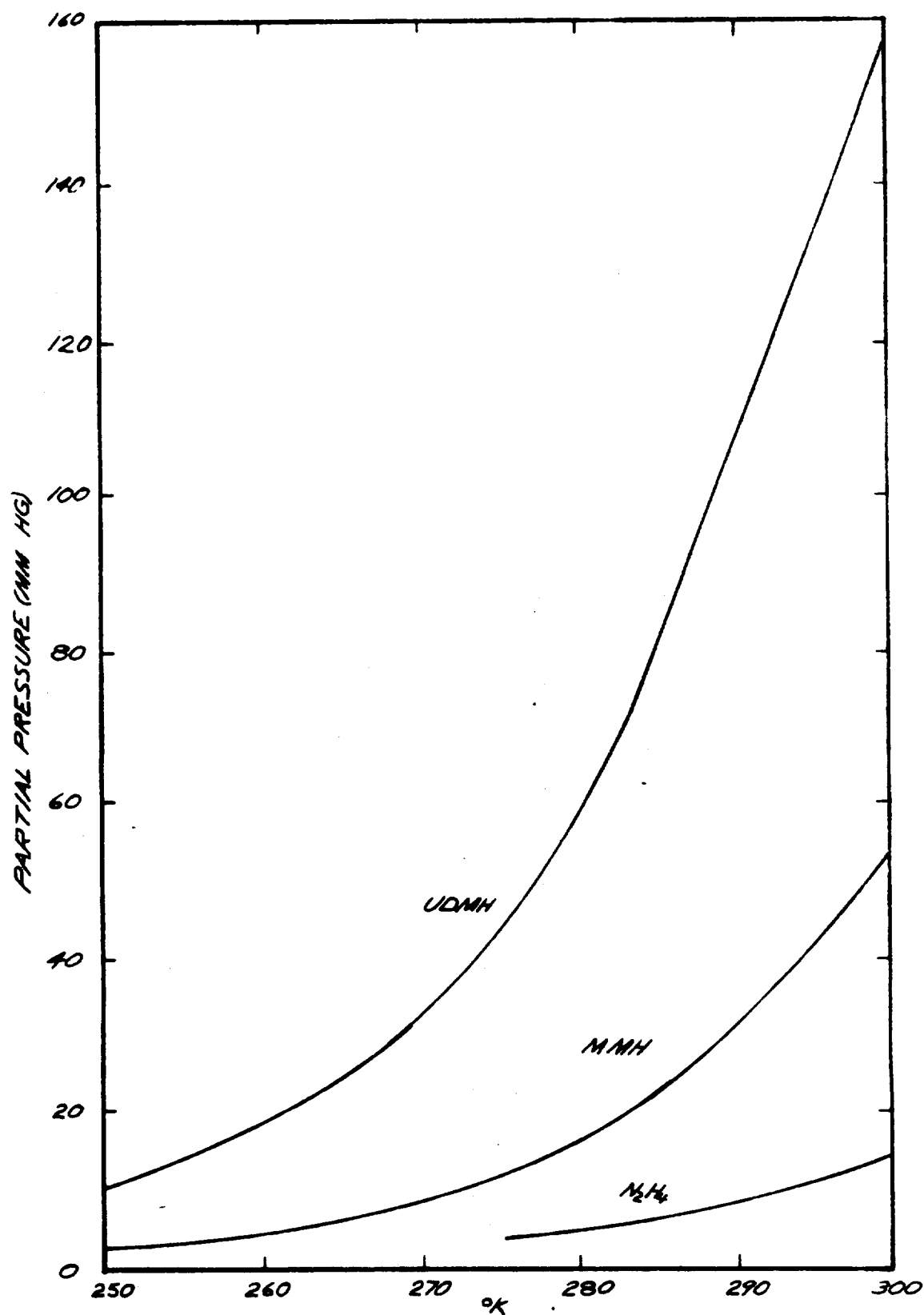


Figure A-1. Liquid-vapor saturation curves for hydrazine fuels

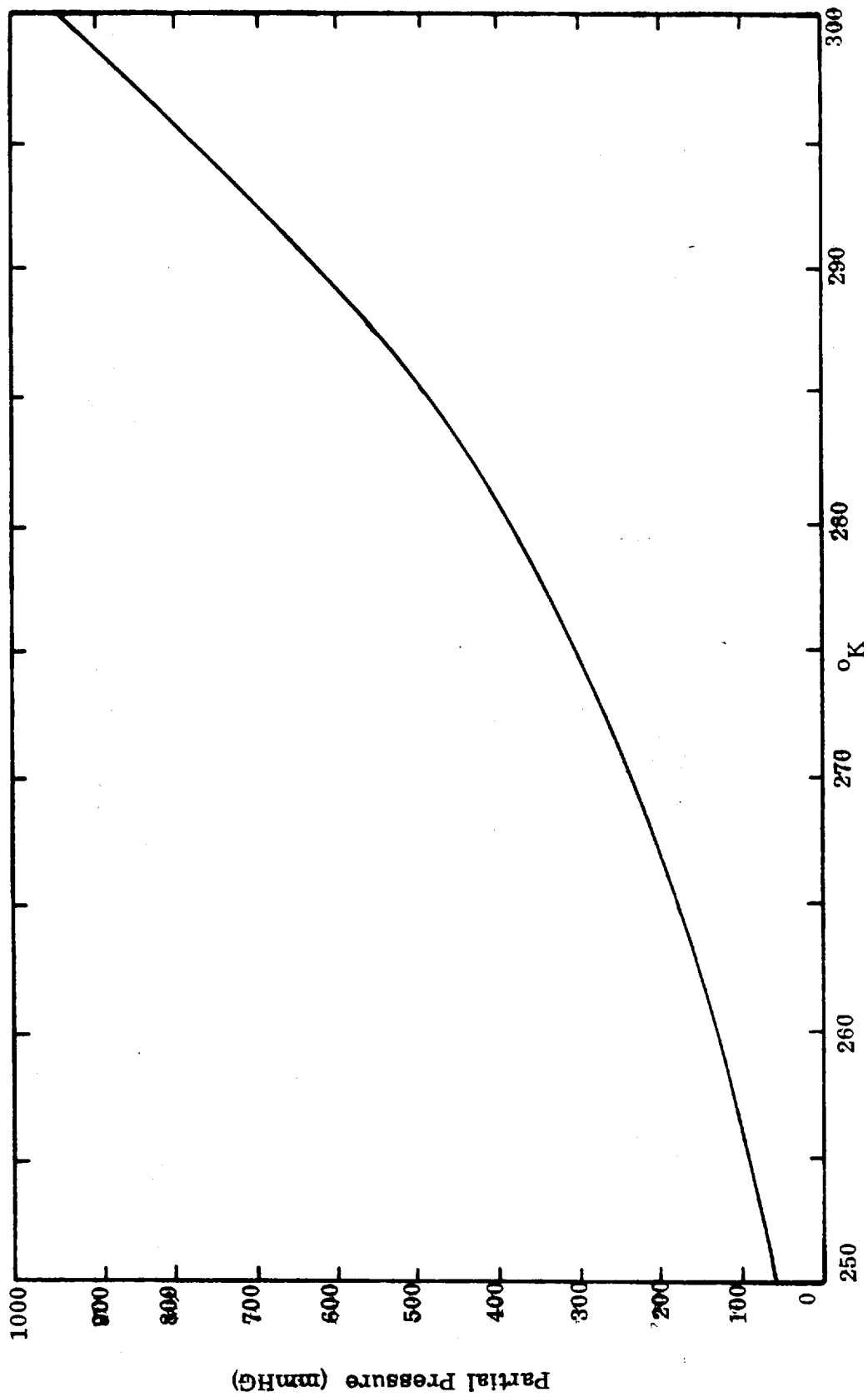


Figure A-2. Liquid-vapor saturation curve for N_2O_4

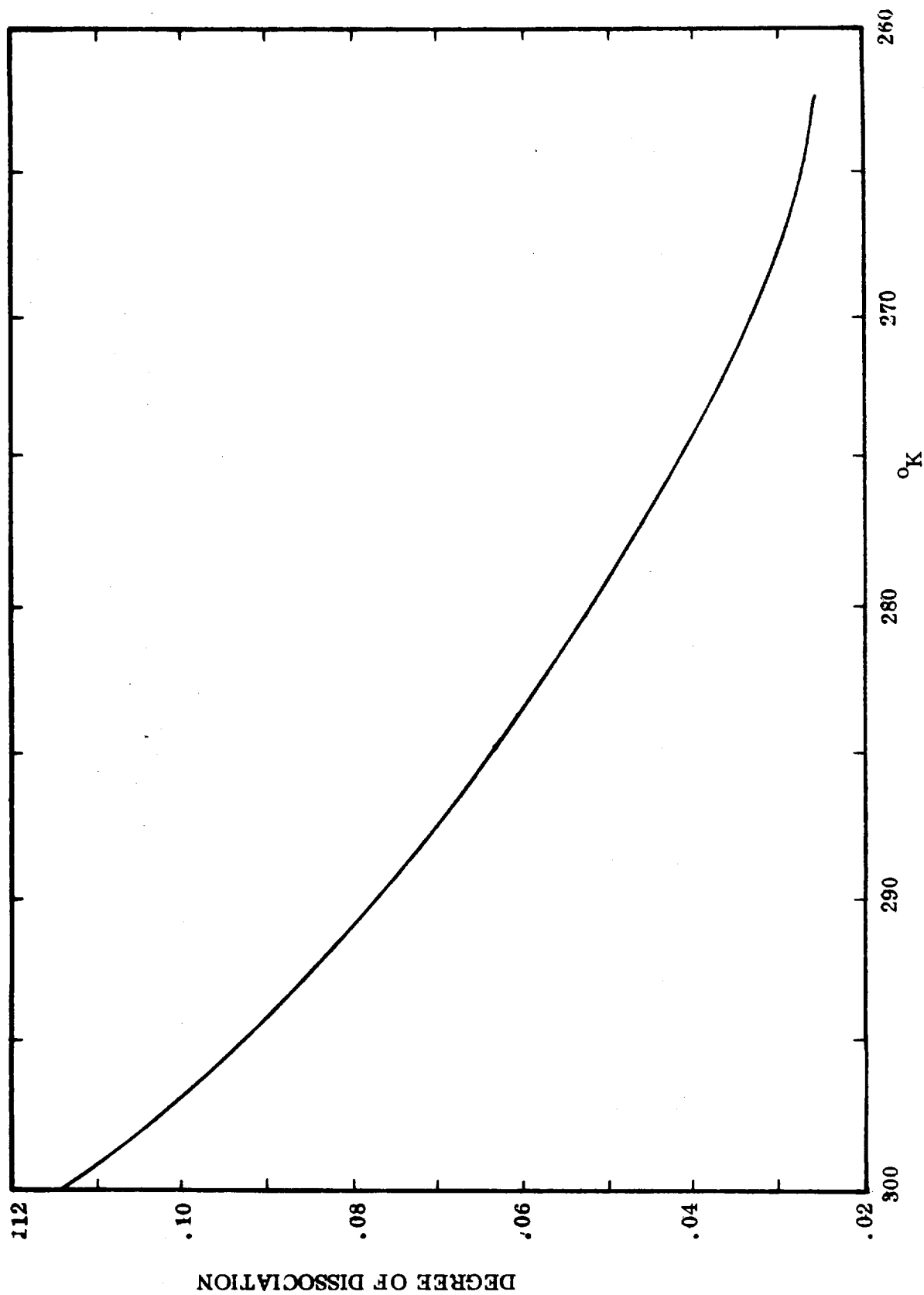


Figure A-3. Degree of dissociation for $\text{N}_2\text{O}_4 = 2\text{NO}_2$, at three atmospheres.

APPENDIX B

MONOMETHYL HYDRAZINE (MMH) ASSAY

Reagents

- (1) p-Dimethylaminobenzaldehyde (DAB) solution
Must be prepared fresh each day
2.0g. DAB, 90 ml. Methanol, and
10 ml. of concentrated HCl
- (2) Standard MMH Solution
1.00g. MMH is diluted to 1.0 liter with
H₂O - stock solution
1 ml. of above stock solution is diluted with H₂O to 100 ml. -
working solution

Procedure - Standard Curve

Into six 10 ml. volumetric flasks, pipet 5 ml. DAB reagent. In order, pipet 1, 2, 3, 4, 5 ml. of working MMH standard and to the sixth flask add 5 ml. H₂O (reagent blank).

Dilute these solutions as needed to 10 ml. with H₂O, mix well and let stand 30 minutes. Determine absorbance on a suitable spectrophotometer at 485 mm.

For sample determination, prepare appropriate dilution to obtain a final concentration in 10 ml. flask of 1.5 micrograms/ml. Use 5 ml. of this solution and 5 ml. of the DAB solution.

APPENDIX C

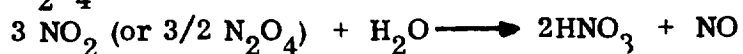
NOTES ON SCRUBBERS

	Page
I. Scrubbing of Nitrogen Tetroxide	
A. Theoretical considerations	312
B. Performance results	314
C. Expert opinions	316
D. Conclusion	318
II. Descriptions of Scrubbers Used for Hypergolic Propellant Vapors	
A. Hamilton Standard's Gemini and Saturn scrubbers	319
B. Hamilton Standard's NASA-Goddard hydrazine scrubber	322
C. The Peabody oxidizer scrubber	324
D. The Nolte hydrazine scrubber	326
E. The Rockwell scrubber system	328

1. SCRUBBING OF NITROGEN TETROXIDE

A. Theoretical Considerations

Dinitrogen Tetroxide (N_2O_4) is the oxidizer of choice in the Shuttle program. N_2O_4 and nitrogen dioxide (NO_2) always exist as mixtures which reach equilibrium rapidly. The relative proportion of each is determined by concentration and temperature, with high temperature and low concentration favoring the formation of NO_2 at the expense of N_2O_4 . Scrubbing of NO_2 - N_2O_4 presents formidable problems because of the low solubility of these agents in water and also because NO is formed during the absorption of NO_2 and N_2O_4 in water according to the following equation:



As nitric oxide is only sparingly soluble in water, oxidation to NO_2 must take place in the gas phase before significant absorption of the evolved nitric oxide can occur whenever more than a few p.p.m. of NO_2 are being absorbed. The oxidation of NO (the rate controlling step in the absorption of low concentrations of nitrogen oxides) is concentration dependent as seen in Table C-I, which shows the time required for half the NO present in air at various concentrations to be oxidized to NO_2 at standard temperature and pressure.

TABLE C-I

OXIDATION RATE OF NO IN AIR

NO conc. in air, ppm	Time for half NO to be oxidized to NO_2 , min
20,000	.175
10,000	.35
1,000	3.5
100	35
10	350 (5.84 hr)
1	3500 (58.4 hr)

Whereas it takes 10 seconds for half the NO to be oxidized to NO_2 when the concentration is 2% by volume in air, it takes nearly 60 hours for half the NO to be oxidized when the original concentration is 1 ppm. The oxidation

rate for all concentrations increases at higher pressure.

It may be concluded from these facts that:

- (1) multistaged absorption equipment with long gas retention times for oxidation of NO between absorption stages is required for the high efficiency collection of nitrogen oxides from flowing air streams;
- (2) it is impossible to reduce effluent concentrations below a few hundred parts per million NO_x in absorption equipment of practical dimension when the entering concentration is in the percent range;
- (3) the effluent NO_x concentration tends to be insensitive to increases in inlet concentrations because of the greatly increased oxidation times associated with lower concentrations of NO;
- (4) addition of neutralizing chemicals (e.g. NaOH) to the scrubbing liquor has little or no effect on absorption rates for NO_x or on overall efficiency in a multistaged absorption unit as back pressure of solute from the solvent is seldom an important resistance to NO_x absorption in air pollution control applications; but use of chemicals may be necessary to reduce waste water volume by permitting recirculation of the scrubbing liquor.

Experiments¹ conducted in an 8.5 inch diameter counter current tower packed with 5 feet of 1/2 inch Berl Saddles indicated that no permanent improvement in NO_x removal results from recirculating an alkaline scrubbing solution because of the inhibitory effect of accumulations of NaNO_2 on the absorption efficiency of the resulting mixture.

The slow oxidation of NO in air can be improved² by adding an oxidant such as KMnO_4 to the absorption liquid so that NO formed during the hydration of NO_2 can be oxidized in the liquid phase (and made water soluble) before it escapes from solution because of its limited solubility. When KMnO_4 was added to the alkaline scrubbing liquor, absorbability increased by a factor of 20% for the operating conditions employed. The principal problem associated with the use of KMnO_4 in absorber scrubbing liquor in addition to the high cost of the chemical is the formation of an insoluble MnO_4 precipitate which can cause fouling of the absorber packings. Perhaps substitution of KMnO_4 with hydrogen peroxide (H_2O_2) would provide the necessary oxidation without any associated residues.

¹ First, N. W. and J. J. Viles, Jr., "Cleaning of Stack Gases Containing High Concentrations of Nitrogen Oxides." Journal of the Air Pollution Control Association, Volume 21, 122-127 (1971).

² Ibid.

B. Performance Results

First and Viles³ also describe the results of a series of tests performed on a 16-stage cross-flow NO_x gas absorber containing 37 micron diameter curled glass packing.

Details of the unit are shown in Figure C-1.

The manufacturer was the Buffalo Forge Company, and the overall configuration is quite similar to that of the Hamilton Standard Gemini and Saturn scrubbers, which were also fabricated by Buffalo Forge. (See Section II. A below for further description of these units.) Each absorption stage had a face area of 1.25 sq. ft. and contained a 4 inch depth of Owens-Corning K-115 curled glass fibers packed to a density of 2/3 pounds per cubic foot. Fifteen stages were wetted with nozzles having an orifice diameter of 0.170 inches, and delivering 2.5 g/minute at 8 psi. The sixteenth stage was operated dry and served as an eliminator to prevent emission of airborne droplets. The nozzles were serviced from a fresh water supply and waste water drained from the sumps connecting the cells to the bottom of the absorber casing. It was intended that the liquid would rise in the sumps to a level well above the drainage holes leading from the compartments and thereby provide effective air seals between the stages.

Performance tests were conducted under a variety of conditions. Provisions were made to measure temperature, flow rate, and the composition of gas and liquid streams entering and leaving the absorber. The following results were obtained:

- (1) Pure N_2O_4 - NO_2 mixtures at gas temperatures from 78 to 132° and scrubbing water temperatures from 40 to 74° were reduced to 30 ppm at exit from the scrubber because with little or no inert gas present, the gas absorber approximated an infinite retention time reactor after the flowing gas volume shrank to very small values.
- (2) In tests in which conditions were held constant except for NO_2 inlet concentration, outlet concentration appeared to be largely unaffected by very large changes in inlet concentration; i.e., in one series of tests a thirteen-fold increase in NO_2 inlet concentration (2000 to 26,700 ppm) produced no significant increase at the outlet. When outlet concentration was plotted on log paper against average gas velocity through the scrubber, the residual concentration appeared

³ Ibid.

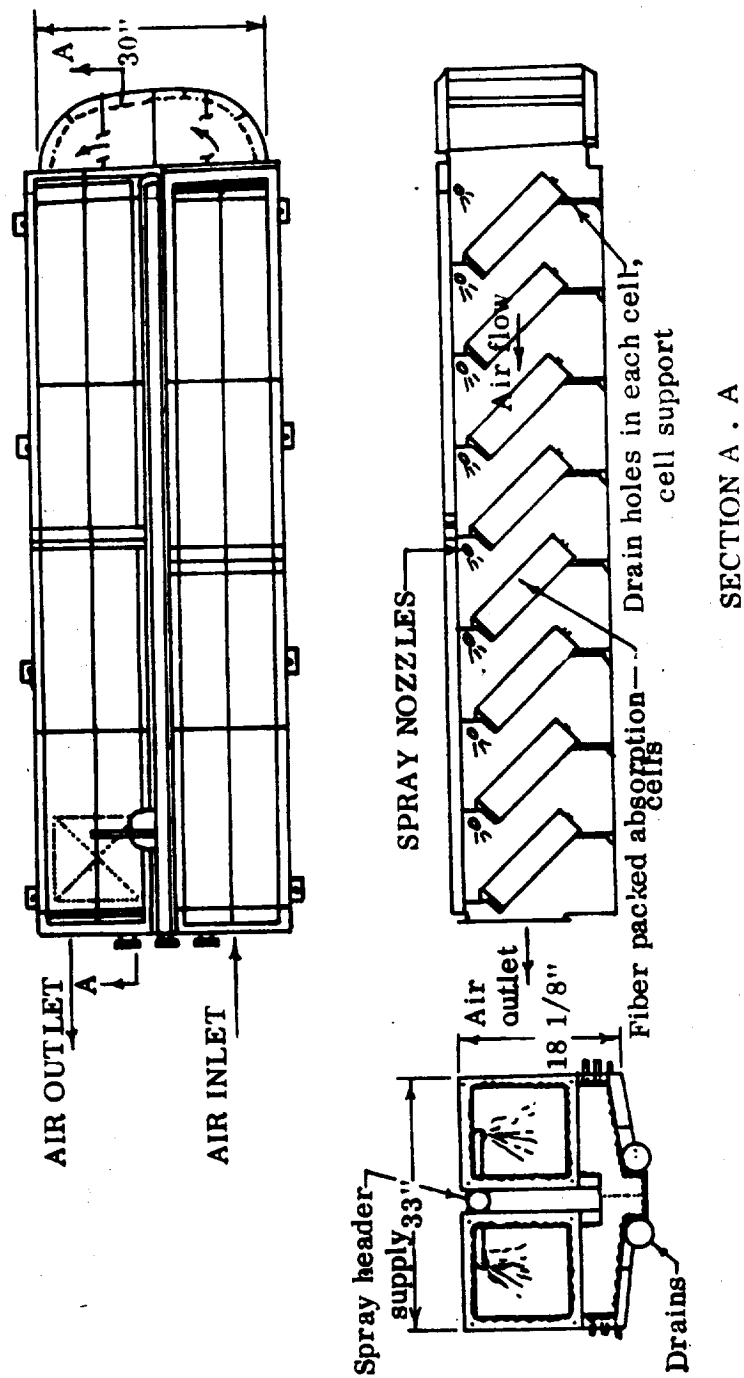


Figure C-1. The Buffalo Forge 16-stage gas absorber tested by First and Viles.

to be approximately proportional to the square of the gas flow velocity.

- (3) The outlet NO_2 concentration increased with a rise in water temperature.
- (4) Pressure of several atmospheres would be required to produce a marked improvement in absorption at low concentrations of NO_2 .

Results of nitrogen oxides removal in the scrubber under a variety of operating conditions are summarized in Table C-II. Known gas volumes were displaced from the scrubber inlet and outlet into dry (previously desiccated) gas sampling flasks by means of glass syringes attached to the flasks. Aliquots of these samples were analyzed for NO_2 and the remainder of each sample analyzed for total nitrogen oxides. Inlet nitrogen oxide concentrations varied from less than 1% by volume to 32.8%. Overall scrubber efficiency varied from slightly over 90% for the lowest inlet concentration to greater than 97% for the highest. In each case, collection efficiency for NO_2 was higher than the efficiency for total oxides and the efficiency for NO was lower.

As the scrubber effluent was diluted with 8000 cfm of essentially NO_x -free air, the resulting concentrations were well below the visible range. In the case of sample 5, total volume entering the scrubber was 110 cfm but 32% (32.8% NO_x inlet concentration and 0.90% outlet concentration) was removed in the scrubber resulting in an effluent volume of 75 cfm. When diluted with 8000 cfm of air, the resulting NO_x concentration at the top of tall stacks was 85 ppm. In the case of sample 3, stack outlet concentration was about 180 ppm.

C. Expert Opinions

Telephone conversations were conducted with the following people connected with scrubber manufacturing or scrubber utilizing firms to determine the current state of the art compared to the previously described scrubbing unit.

NAME	FIRM	PHONE NO.
Dr. Hann Senti	Hoffman LaRoche	201/235-5000
Mr. Ed Hanf	Ceilcote	216/243-0700
Mr. Harry Crumbling	Corning Glass	607/974-7726
Mr. Gray	Allied Chemical	315/468-1611
Mr. Vern Paturka	Ceilcote	216/243-0700
Mr. Allan Quimby	Buffalo Forge Co.	716/847-5258
Mr. Jerry Brewer	U. O. P. Air Correction Div.	203/655-8711
Mr. Robert Soles	Heil Process Eqpt.	813/381-0191

TABLE C-II

Test results obtained by First and Viles: Decontaminating off-gases from metal dissolving with HNO_3

Sample No.	Acid bath conditions		Reaction Rate	Total cfm to ab-sorber	Inlet ab-sorber	Total nitrogen oxides % Outlet ab-sorber	Ab-sorber effc.	Nitrogen dioxide				Nitric oxide, %		
	Conc'n %	Temp						Inlet absorber		Outlet absorber		Ab-sorber effc. %	Inlet ab-sorber	Outlet ab-sorber
								% by vol.	total NO ₂	% by vol.	total NO ₂			
1	15	Room	A*	110	7.35	--	--	4.30	61.0	.137	--	2.85	--	--
2	35	Warm	B*	165	.845	.0822	90.3	.460	54.0	.0260	31.5	.385	.0562	85.4
3	50	Hot	A*	165	9.60	.932	90.3	5.91	61.5	.300	32.0	3.69	.635	82.8
4	50	Warm	C*	110	5.63	.417	92.6	4.87	86.5	.193	46.5	.760	.226	70.2
5	60	Hot	D*	110	32.8	.900	97.3	19.0	58.0	.367	41.0	13.8	.533	96.1

* A = Fairly vigorous

B = Quiescent

C = Passivated with salt accumulations

D = Very vigorous

The conclusion of all these representatives was that no recent advances in the state of the art in scrubbing would enable practical absorption below 100 ppm of oxides of nitrogen.

D. Conclusion

Multistage gas absorption of 1-50% nitric oxide, nitrogen dioxide, and nitrogen tetroxide from air with water or caustic solutions can produce colorless stack discharges. The rate at which NO is oxidized to NO₂ in the gas phase and the solubility rate of NO₂ in water or solution are highly concentration dependent so that reduction of emissions of nitrogen oxides below approximately 200 ppm appears to be impractical. However, high efficiency scrubbing combined with elevated discharge of the cleaned, colorless gases would be an acceptable method of control for ventilated hypergols.

II. DESCRIPTIONS OF SCRUBBERS USED FOR HYPERGOLIC PROPELLANT VAPORS

A. Hamilton - Standard's Gemini and Saturn Scrubbers

Hamilton Standard provided fuel-handling systems for the Gemini and Saturn programs which included scrubbers for the removal of hypergolic propellants which would otherwise be vented to atmosphere. Gaseous nitrogen-bearing fuel or oxidizer vapors (different scrubbers of the same design were used for fuels and oxidizers) were put through the scrubbers, which met design specifications calling for contaminant concentration of less than 5 ppm N_2O_4 or less than 1 ppm MMH at the outlet of the system. This outlet is downstream of a dilution fan/mixing chamber where the scrubber effluent is mixed with fresh air in a 100:1 ratio, thus reducing contaminant concentrations by a factor of one hundred.

The scrubbers were engineered to accept up to 10 SCFM of up to 10^6 ppm N_2O_4 or MMH (up to 10 SCFM of fuel or oxidizer vapor pure) or to accept up to 60 SCFM of up to 1500 ppm N_2O_4 or MMH contaminated nitrogen. One may infer that the scrubber, operating with a through flow of 60 SCFM, must reduce N_2O_4 concentration by at least a factor of 3 (67% removal) or must reduce MMH concentration by a factor of 15 (93% removal).

Scrubbing is accomplished by a cross-flow absorber which moves the gas across sixteen cascaded filters, each with an associated fresh water spray nozzle. The cross-section of the scrubber is about $2/3 \text{ ft}^2$ and of each filter, about 1 ft^2 . The filters are of pyrex glass wool supported by stainless steel. The length of the scrubber is about 18 ft., folded once to a "U" form. Water flow rate is 40 GPM. The scrubber and also the associated dilution blower were provided by the Buffalo Forge Co. of Buffalo, N. Y.; test results were described in Section I. B above. Schematic diagrams are shown in Figures C-2 and C-3; see also Figure C-1 above.

We wish to acknowledge the efforts of Mr. J. H. Vanderbilt, Chief of Preliminary Design, Industrial Products and Services, Hamilton Standard, in providing the foregoing information.

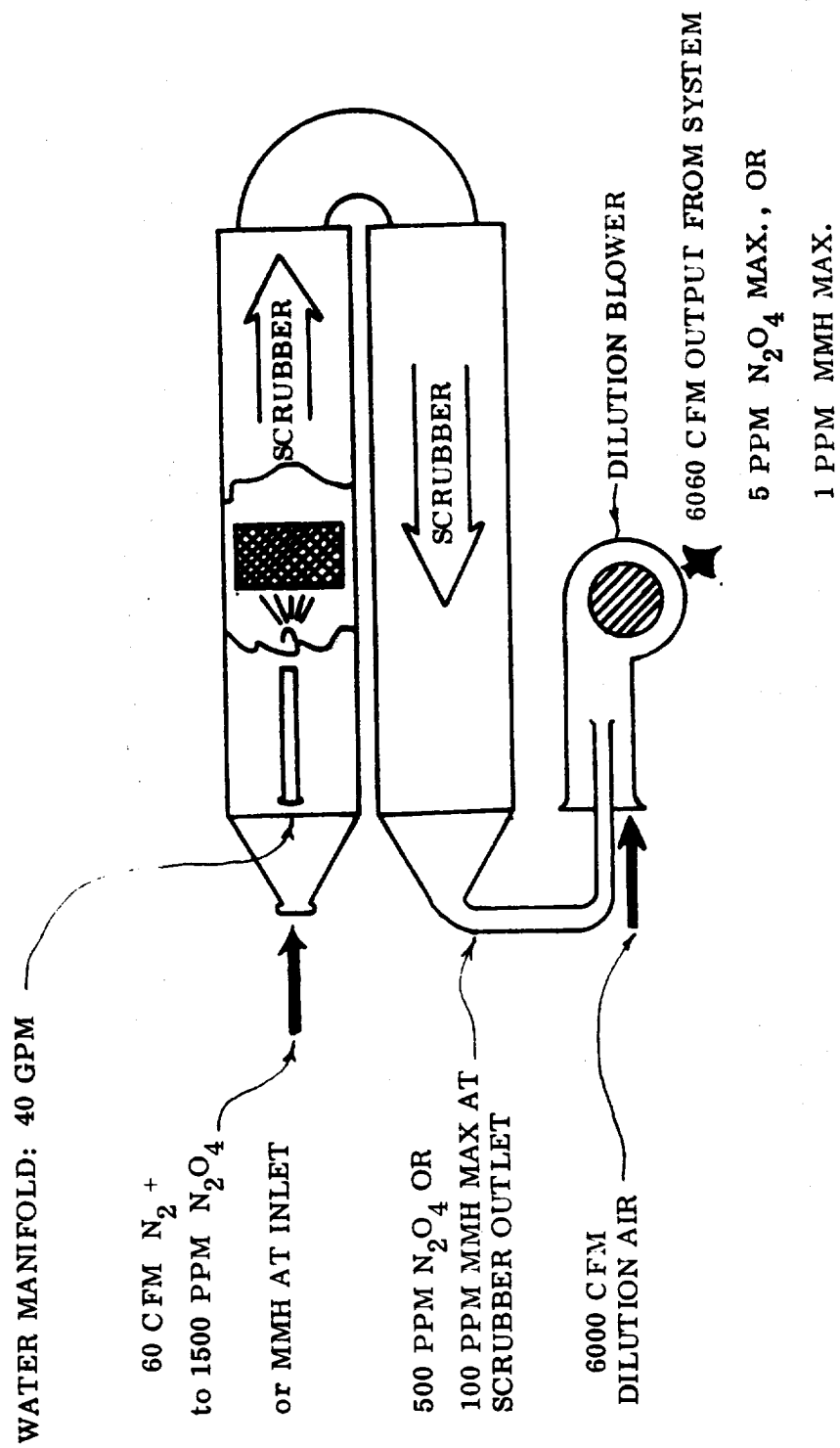


Figure C-2. Top View of the Hamilton Standard (Buffalo Forge) scrubber.

SCRUBBER DIAGRAM

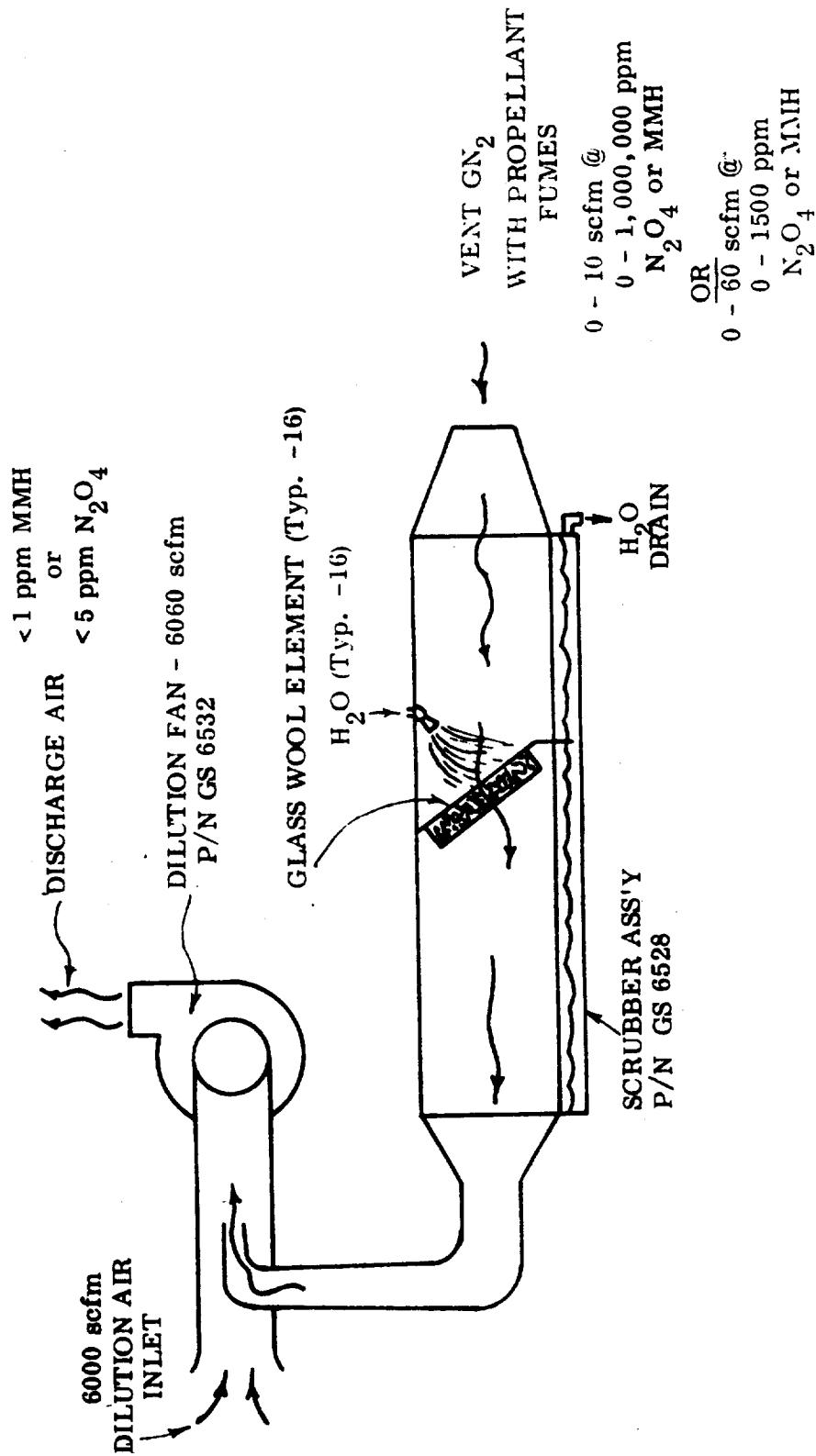


Figure C-3. Side view of the Hamilton Standard (Buffalo Forge) scrubber.

B. Hamilton Standard's NASA-Goddard Hydrazine Scrubber

More recently, Hamilton Standard completed for NASA - Goddard a small scrubber-neutralization system to allow the indoor firing of mono-propellant hydrazine reaction rockets. The system will accomodate a single 5 lb. thrust engine and two 1/2 lb. thrust engines simultaneously, representing a hydrazine flow rate of .025 - .030 lbs/min. The contaminant level in the system outlet is not known. Exhaust from the test engine(s) is drawn into a manifold along with a significant quantity of room air, which has the purpose of diluting any free hydrogen which may present danger of explosion otherwise. The depression to draw the exhaust into the manifold is provided by coupling the manifold outlet to the inlet of a jet pump scrubber, which is a large water-driven jet pump. The scrubber exhaust impinges on the free surface of 100 gallons of liquid in an oversize water box; the liquid is a weak (pH 2.2) solution of hydrochloric acid (HCl). Gas and liquid are separated in this box and the cleaned gas is vented. The jet pump scrubber, drawing manifold gases, has an 8 in. (diameter) throat, or venturi, and the water jet which powers the scrubber uses about 50 GPM at 70 PSI, requiring an approximate 15 HP motor to drive the water pump. The jet pump scrubber is supplied by Croll-Reynolds of Westfield, N. J., and is of a type commonly supplied by this company, if not actually "off-the-shelf".

A diagram of the jet pump scrubber is shown in Figure C-4. We wish to acknowledge the efforts of Mr. R. H. Hall, Operations Manager, Space Systems Dept., and Mr. J. Lynch and Mr. H. R. Heilman, all of Hamilton Standard, Windsor Locks, Conn., in providing us with the foregoing information.

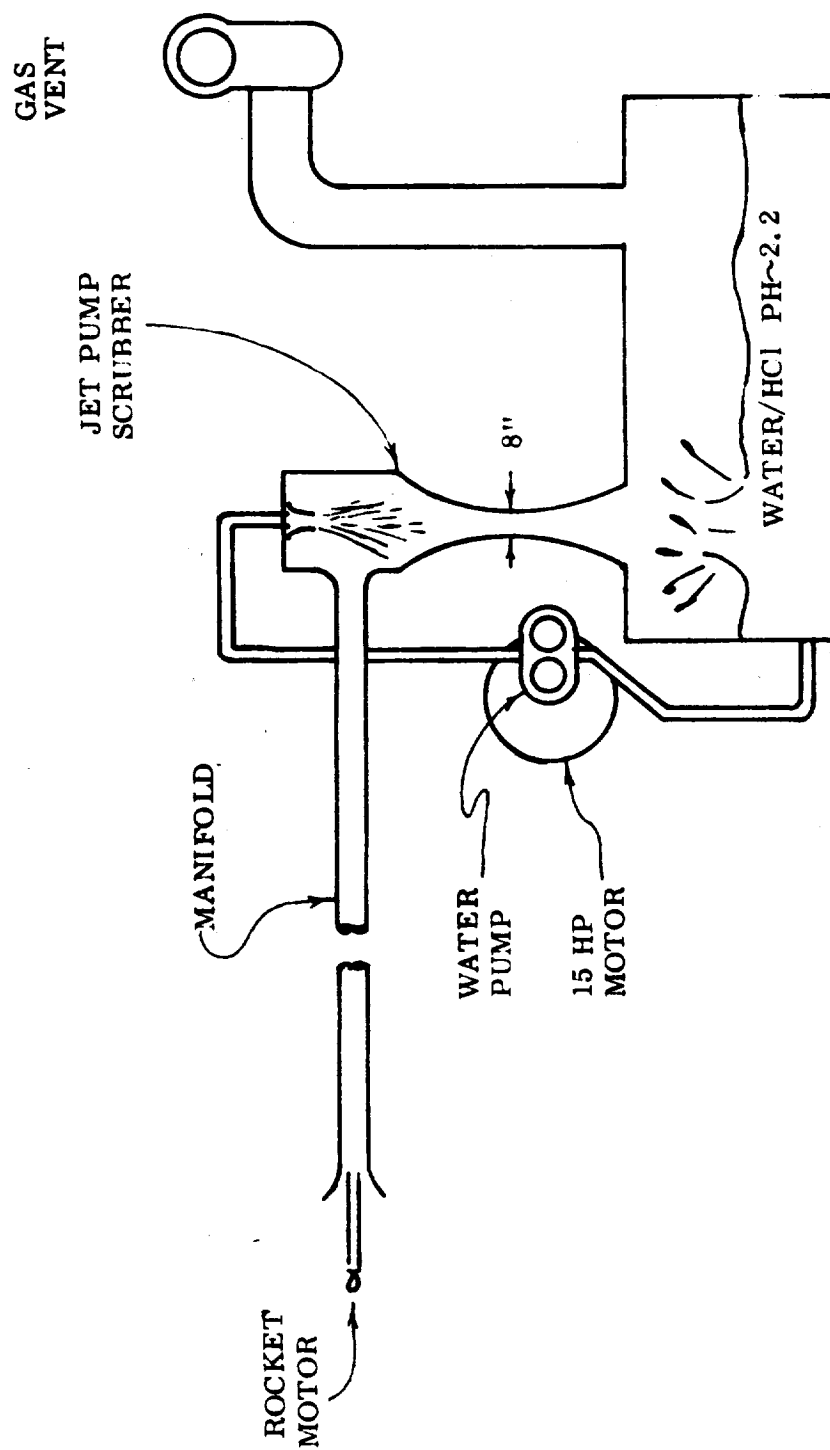


Figure C-4. The Hamilton Standard (Croll-Reynolds) jet pump scrubber.

C. The Peabody Oxidizer Scrubber

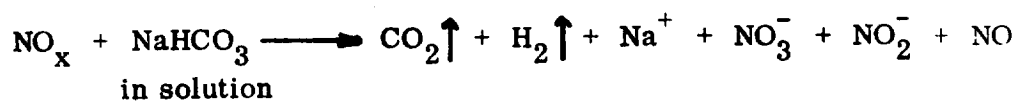
Peabody scrubbers have been installed on the N_2O_4 vent lines at the Delta launch facilities at both Cape Canaveral and Vandenberg Air Force Base. The purpose of this section is to briefly describe these scrubbers.

The Peabody scrubber consists of a column approximately 9 inches in diameter mounted on a larger base approximately 3 ft. in diameter containing a 5% solution of NaHCO_3 which is recirculated during operation. Within the column are 5 impingement baffle plates located at different levels, a spray header in the upper part of the column, and a spray nozzle in the lower part to saturate the incoming gases and to cool the bottom plate stage, and a stainless steel wire mesh water demister at the top of the column.

The liquor recirculating pump, gas control system, and the necessary regulating and safety valving and piping are located externally. The whole apparatus is mounted on a trailer for portability.

The recirculating pump capacity is 24 gpm; the GN_2 gas control regulates pressure within the system to smooth out pressure surges and partial vacuums and to control the operating pressure.

The base and piping hold about 190 gallons of scrubber solution, and a float-type liquid level controller adjusts the water level on the plates. The vent vapors enter near the top of the base of the scrubber where they encounter the NaHCO_3 solution spray. The reaction begins here and continues as the gas proceeds through the 5 stages of baffles, as follows:



with incidental NO formation:



The NO reacts with the HCO_3^- ion, dissolves in water or is vented from the column.

The final products in the scrubber liquor are solutions of NaNO_3 , NaNO_2 ,

and unreacted NaHCO_3 , with varying amounts of dissolved gases. Excess CO_2 , H_2 , H_2O -vapor, and NO_x are released to the atmosphere.

The water for scrubbing is supplied by the spray head located above the top plate stage. As the gases rise through the column they come into intimate contact with liquid flowing downward through the five stages of impingement baffles, utilizing a system of down comers and seals. In the process, the gases are entrained as myriads of small bubbles, with an immense surface area, thus enhancing absorption into the water layers on the baffle plates.

As the water trickles down the column, it eventually reaches the enlarged base (reservoir) and is recirculated by the pump. Replacement of the scrubber liquor is performed as required.

The water demister captures entrained liquid droplets from the scrubber gas, forming larger drops which can fall downward.

The cleaned gas (usually N_2) exits through a pressure-reducing valve, located on the top of the column, to the atmosphere. A safety valve located atop the scrubber base prevents a build up of excessive pressure within the system.

Except for the pump, this scrubber has no moving parts. The necessary maintenance reported by its users consists primarily of unclogging plugged spray heads and occasional replacement of the liquid solution.

The efficiency of this unit is not known. Only minor visible brown plumes were reported on rare occasions by the personnel involved.

D. The Nolte Hydrazine Scrubber

Nolte scrubbers have been installed on the Aerozine 50 vent lines at the Delta launch facilities at both Cape Canaveral and Vandenberg Air Force Base. The scrubber schematic is shown in Figure C-5, and the following brief description is quoted from an operating manual.

"The Scrubber Water Supply Regulator feeds 30 psig, 3 G. P. M. tap water to the Scrubber through a motor-operated, normally-closed ball valve. The Scrubber Water Supply Valve is opened at the beginning of every test by turning on S-5 at the electrical control panel. Water then flows through the Scrubber Flow Valve, and Scrubber Spray Valve. These valves control the scrubbing efficiency of the unit.

"A standpipe in the bottom of the scrubber controls the liquid level for optimum system back pressure, and a Scrubber Drain Valve allows complete draining when required. Contaminated gas enters at the vapor inlet and rises through the water spray to the 1st scrubbing stage. As the gas flows through the 15 3/16" holes it comes in contact with the baffle and is deflected down against the water flooded plate. The water is thus aerated and subsequently absorbs and neutralizes the harmful propellant fumes in the vented gas. After the gas has passed through four successive scrubbing stages, 90% of the noxious vapors are removed; the water vapor is screened out with a stainless wire-mesh water eliminator, and the remaining gas is vented to atmosphere. To prevent high-pressure surge damage, each scrubbing stage has a 3/4 inch standpipe welded into it with a water cup on the bottom. When the pressure builds up, the water blows out of the cup and allows gas to flow straight to the vent without passing through the scrubbing holes. Water refills the cup after the pressure surge is reduced."

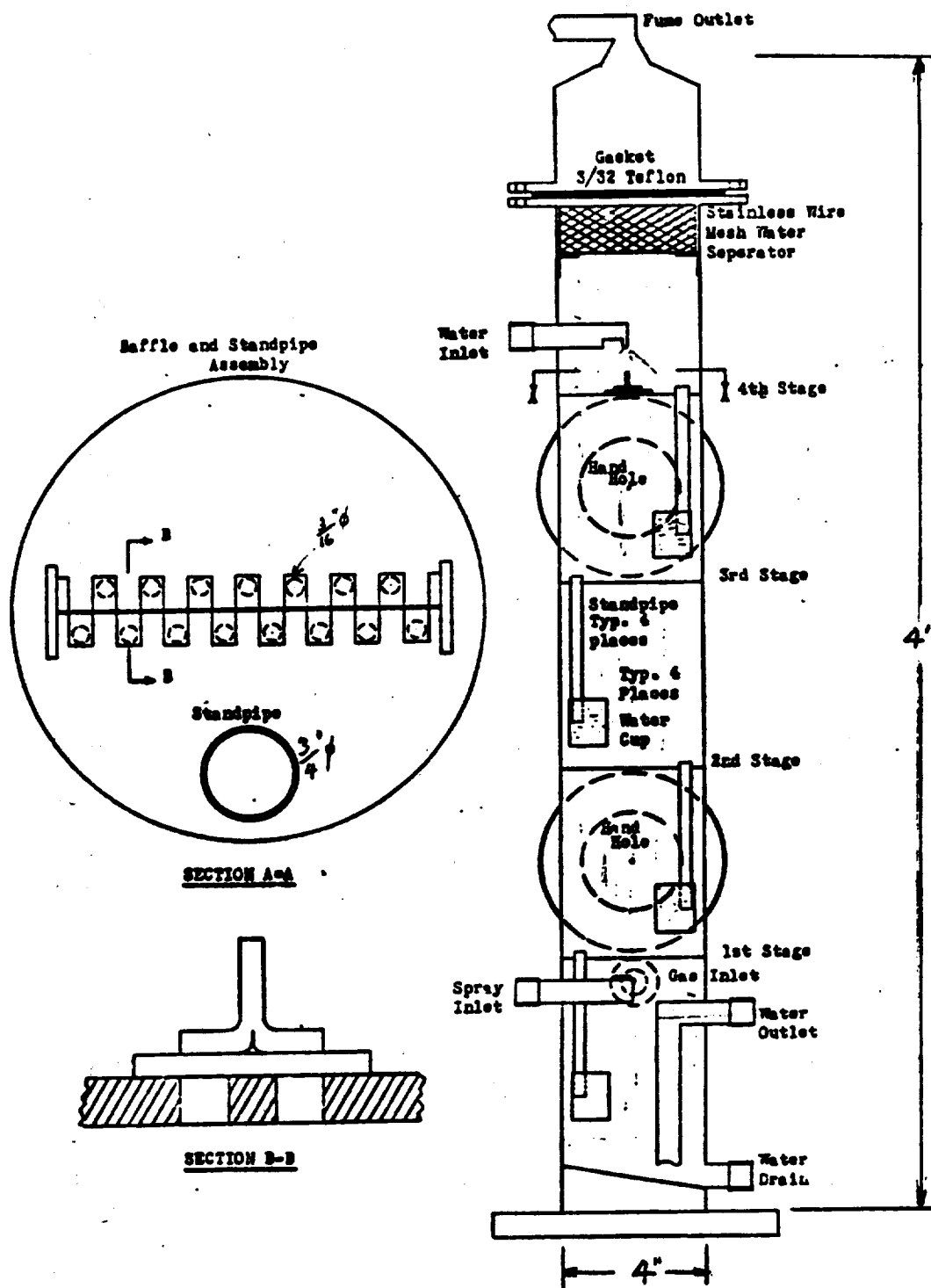


Figure C-5. The Nolte propellant vent scrubber.

E. The Rockwell Scrubber System

A system of scrubbers for N_2O_4 vapors was designed and built at the Space Division of North American Aviation (now Rockwell International) in the late 1960's. The following paragraphs describe the system.

"The RCS facility cell exhaust system employs three exhaust systems that can operate independently or in several combinations. Two of the systems, located adjacent to fuel and oxidizer test cells, have identical hardware. They employ 2000-cfm-rated exhaust fans, drawing approximately 1600 cfm from the test cell and 400 cfm from the 6 by 6-foot storage room at the corner of each propellant cell. The other system is serviced by one 6000-cfm-rated exhaust system.

"The ducting from the 6000-cfm scrubber is designed to draw exhaust gases from either the command module, service module, or both test cells. The fuel cell scrubber is interconnected to the fuel, fuel storage, service module, and command module cell. The oxidizer scrubber is connected to the oxidizer, oxidizer storage, and command module cells. All positions can be independently serviced.

"Each of the three exhaust systems consists of interconnecting ducting, a cyclone exhaust scrubber and a contaminants dilution unit equipped with an axial fan. The interconnecting ducting for the cells is equipped with remotely operated draft and isolation dampers, designed to the same principle as the forced air supply, i.e., selective isolation. In addition to the cell isolation capability, the scrubbers are equipped with dampers located in the ducting near the intakes to the exhaust fans; these dampers can be used to isolate the scrubbers from the cells or for selectivity metering the exhausting from the cells.

"Each of the cyclone exhaust scrubbers consists of an intake fan and three water fog chambers (stacked). The fog chambers are separated by woven stainless steel screens and are equipped with separate air-water fog spray systems. The mechanism of the exhaust scrubber essentially involves forcing the contaminated air, exhausted from the cell, through the fog chambers, where they chemically react, and out to the contaminants dilution unit. In the contaminants dilution unit, the contaminated exhaust is diluted by mixing with uncontaminated air. It is exhausted through an outlet stack into the atmosphere at a high velocity, so that it is carried away from the vicinity of the facility roof top.

"The contaminants dilution unit consists of a high-speed (10,000-cfm-rated) axial fan installed in a cylindrical stack. The stacks are equipped with baffles; the baffles create eddy currents and provide ultimate mixing of uncontaminated air and air contaminated exhaust from the scrubber outlet before projecting them into the atmosphere. The contaminants dilution unit is installed adjacent to, and above, the exhaust scrubber unit. It is connected at the outlet of the scrubber unit and the inlet to the axial fans on a tee arrangement, so that the fresh air intake is not appreciably restricted, yet the exhaust gases existing from the scrubber is entrained and accelerated.

"The water, used in the fogging system, is supplied by a pump and is drawn from a water-level controlled reservoir. After the water is fogged into the chambers, it makes contact with the propellant vapors and chemically reacts. (Note: the exhaust from the scrubber fan is forced through the water fog in a swirling, cyclonic motion which, in conjunction with the three fog chambers, provides a large contact area for the reaction and scrubbing of the gases.) The residual falls to the bottom of the scrubber chamber and drains into the facility sump where it is later neutralized and loaded into the city sewage."⁴

"The chemical reaction of the propellants with water are second-order homogeneous reactions; the completion of the reactions depend solely on the length of contact time and assurance of excess water. However, since the first phase of the reaction is evolution of additional gas, care must be taken to insure that the fumes are not pushed through the scrubber at a rate which does not allow sufficient reaction time.

"In the present scrubber design, the reaction time is assured by a design using three fog chambers. As the metered exhaust fumes are forced tangentially into the scrubber chamber, they come into contact with water fog in the first chamber. At the top of this chamber, approximately at the one-third level of the scrubber, is a core buster. After the primary reaction, the resultant enters the second fog chamber and further reacts. Fumes escaping the second chamber enter the chamber for further scrubbing action.

⁴ Freeman, B., "The Reaction Control System Facility Operational Capabilities Evaluation and Analysis." Report No. SID 66-1905, North American Aviation, Inc., Space Division, Downey, Calif., May 1967, pp. 33-34.

"The calculated efficiency of the first chamber is 50 percent provided that the correct metered level of intake is used. If necessary the total scrubber can be operated at an 87.5 percent efficiency. The escaping fumes are then diluted by mixing with uncontaminated air in the contaminated dilution unit and exhausted to the atmosphere."⁵

⁵ Op. cit., p. 46.

APPENDIX D

SPECIAL NOTES ON HF REMOVAL FROM EFFLUENT STREAMS

Although the problem of HF content in IRFNA disposal effluent is a relatively minor one in terms of absolute quantities involved, it proved to be perplexing because of the difficulties we experienced in completely removing the fluoride. The purpose of this appendix is to present late developments (after the main report was completed) and some additional discussion of the problem.

Dr. Robert S. Ottinger, Head, Chemical Engineering Design and Analysis Section, TRW Systems, Redondo Beach, California, had commented earlier on the fact that HF disposal activities are ongoing at TRW in connection with laser activities. When asked for further details, he wrote as follows:

"The HF laser system exhausts its gases through a steam ejector system which acts very similar to a venturi scrubber. The water ejected in the latter stages of the ejector is alkaline, forming soluble salts with the absorbed HF. The liquid effluent from the ejector is passed through a limestone packed bed which fixes the fluoride ion as highly insoluble calcium fluoride. The water from the process, which is virtually free of fluoride ion, is put into a holding pond and used as process water."¹

At about the same time, our own experiments with HF removal were being continued in an attempt to find a precipitating reagent that would be more effective than the CaCl_2 and $\text{Ca}(\text{OH})_2$ reported on in Section V of the "Application Studies" portion of this report. $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ were both investigated, with results not substantially different from those found previously. These experiments were performed using pH controllers to adjust the pH of solution all the way from 1.2 to 12.5, with the problem of limited precipitation persisting at all pH levels, for all of the precipitating agents.

Further study led us to the conclusion that the problem lay in the presence of high concentrations of nitrate ions, NO_3^- , which increase the solubility of the CaF_2 to the point where only a portion precipitates out.

¹ Ottinger, R. S., Private Communication dated 25 October 1974.

This problem would not occur in normal industrial practice where HF is removed from effluent streams in which CaF_2 is virtually insoluble, but seems unavoidable in our case where the HF is used as an inhibitor in nitric acid.

Our final conclusion, in view of these developments, is twofold. First, it appears that a packed limestone (calcium carbonate) bed, as discussed in the main body of the report, should be effective in precipitating HF from IRFNA solutions as well as neutralizing the nitric acid. Second, the percentage of HF precipitated will be limited, with calcium carbonate as well as with the other calcium compounds, due to the effect of the nitrate ions on the solubility of CaF_2 . Due to the small absolute quantities of HF involved, we do not regard this problem to be an especially serious one.

2

3

4